In Appendix 3 of Ethyl's submission, data was reported on two 1989 Ford Crown Victorias equipped with 5.0L engines and dual split-bed, close-coupled catalyst systems. The cars were operated for 25,000 miles at speeds up to 65 mph and then an additional 10,000 miles at speeds up to 80 mph. The driving condition was selected to demonstrate that HiTEC 3000 does not cause or contribute to emission system failure. Results of this test show that even under prolonged high speed, high temperature driving conditions, use of the additive at the concentration requested does not adversely affect catalyst operation.

At the completion of the program the catalytic converters were removed from the respective vehicles and installed on a slave vehicle. This vehicle, a 1989 5.0L rental car, was used to generate the exhaust gases for the conversion efficiency measurements reported below in Table II. These conversion efficiency results coupled with the back pressure results reported in Appendix 3 of the waiver clearly demonstrate that the use of the Additive has no detrimental effect on catalyst performance.

TABLE II

Ethyl High Speed Test

	Conversion Efficiency, %		
Fuel	HC	CO	NOx
Clear	91.4	94.6	59.4
H-3000	92.1	94.3	58.5

In an effort to monitor the performance of Canadian vehicles operating on gasoline containing HiTEC 3000, Petro-Canada has an ongoing program. This program was reported in their submission to the waiver docket.[19] Included in their program are a variety of employee vehicles of which photographs of a catalyst from a 1986 3.0L Ford Taurus may be found in Attachment 2. This vehicle had accumulated 170,000 km (102,000 mi) of consumer service prior to the emission testing reported in Table III.

The pictures show manganese deposits on the catalyst, but as noted below, the vehicle easily met the Canadian standards applicable to 1986, and considering its mileage, would most likely have met current U.S. standards at 50,000 miles.

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[19]See Petro-Canada submission.

TABLE III

1986 Ford Taurus - Petro-Canada Study

Mileage	HC	CO	NOx
	Emissions, gm/mile		
102,000	0.57	5.93	1.77

III. Ford Comments on Test Protocol

Ford commented that Ethyl's mileage accumulation fuel did not contain a deposit control additive package. They said that the "Lack of fuel detergents would cause an increase in the combustion chamber or intake valve system deposits and thereby result in an unrepresentative baseline as a reference point."

As shown in Appendix 1, Attachment 1-3, of Ethyl's Waiver Application, Howell EEE fuel meets rigid specifications. It contains very low concentrations of olefins, which are suspected of being a major cause of deposits on fuel injectors and other engine parts. Because of its inherent stability, an additive package is unnecessary to protect against fuel deposits.

This was demonstrated in Ethyl's fleet test program, based on average engine-out emissions for the vehicles on clear fuels. Hydrocarbons, carbon monoxide and nitrogen oxides showed only minor changes between the start-of-test at 1,000 miles and end-of-test at 75,000 miles (Table IV below).

TABLE IV

AVERAGE ENGINE-OUT EMISSIONS
Ethyl Fleet Test Data

Mileage	HC, g/Mile Clear	CO, g/Mile Clear	NOx, g/Mile Clear
1,000	2.157	10.32	2.18
75,000	2.102	10.78	2.26

The small change in emissions over the 75,000 mile program shows that Howell EEE fuel could not have caused the formation of deposits in the test vehicles. Additionally, driveability would have deteriorated substantially if vehicle fuel injectors had plugged. In Ethyl's test fleet, the driveability problem never arose because of improved injector design and the overall stability of Howell EEE.

Therefore, there is no validity to Ford's claim about a lack of a detergent resulting in an unrepresentative baseline for emission measurements.

Photographs of the fuel injectors removed from cars D-3 and D-4 illustrate the absence of fuel injector deposits (Attachment 3). As illustrated, at the end of 50,000 miles of operation none of the injectors have significant deposits in the pintle area. The black specks depicted on injectors D-3 (#1) and D-4 (#6) are probably carbon residue which broke away from the edge area.

The absence of intake valve deposits is depicted in the photographs of Car C-6 (Attachment 4). This vehicle had operated a total of 75,000 miles. As illustrated, the level of deposits is very low and not unlike that of a high quality detergent gasoline. For comparison purposes, a photo is provided of the intake valves from a test using a commercial gasoline containing a detergent.

Regarding the lack of light duty truck data, existing LDT standards are much higher than passenger vehicles (Table V). Although we do not have data from a truck, we do have the high speed vehicle data which indicates no plugging and good conversion efficiency in a close-coupled system with a relatively large engine.

TABLE V

U.S. Emission Standards

Light-Duty Truck

(gm/mi)

Year	HC	CO	NOx
Post-1985	0.8	10.0	2.3

IV. Ford Comments on HiTEC 3000 HC Effect

Ford has questioned why the adverse effects of HC emissions that were demonstrated in studies conducted in the late 1970's with 1/8 and 1/16 gm Mn/US gallon are not so readily apparent in the most recent Ethyl test program at 1/32 gm Mn/gallon.

It is a well known fact that since 1978 emission control and engine management technology has dramatically improved. Since the 1978 studies were completed, automobile emission control systems have been equipped with three-way catalytic converters. The three-way catalytic converter combined with lambda closed-loop control is the most effective pollutant-reduction system presently available.[20] The evolution from open loop carburetor systems to closed loop electronic fuel injection systems has greatly reduced the variability in air/fuel ratio.

The chemistry of the exhaust gas is most appropriate to reactions at the point of stoichiometry.[21] A prerequisite is that the air-fuel mixture supplied to the engine, and thereby the exhaust is at the stoichiometric ratio.

The improvement in emission control technology is apparent when the average hydrocarbon conversion efficiency of the catalytic converters from the 1978 CRC data is compared to the recently submitted Ethyl fleet data. At 50,000 miles the HC conversion efficiency of the CRC data averaged approximately 77 percent compared to 85.9 percent for the Ethyl fleet.

The overall improvement in tailpipe emissions is further substantiated by the decrease in average in-use hydrocarbon emission levels. The EPA has reported average HC emissions of approximately 2.5 gm/mile in the 1977-79 era, and approximately 0.7 gm/mile in the 1980-82 period.[22] General Motors has reported continued improvements in their fleet from 0.67 gm/mile in 1981 to 0.28 gm/mile in 1986.

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[20]Automotive Electric/Electronic Systems, Robert Bosch.

[21]Developments in Emission Control Technology for Vehicles: A Challenge for Catalysts, The Science of the Total Environment, 93 (1990). See Figure 8, p. 236.

[22]U.S. Light Duty Vehicle Fleet Emissions Performance and the Emissions Impact of Technology Changes, SAE Paper 881681.

In SAE paper 881682, General Motors states that the reasons for the improvement were:

Improved fuel metering mainly due to increased use of fuel injection;

Improvements in the high mileage performance of catalytic converters;

Continuous improvement in control algorithms, strategies, and calibrations, and;

Improved system and component reliability.[23]

Because of these vast improvements in emission control technologies, the emission results of studies conducted on vehicles equipped with outdated technology are not relevant to this discussion.

V. <u>Ford Comments on NOx Reduction</u>

Ford states "There appears to be no definitive explanation for the NOx reduction," but acknowledges that Mn_3O_4 does coat the interior of the exhaust system and that Mn_3O_4 does "indeed have the ability to catalytically decompose NOx." The only statement they offer to refute the assertion by Ethyl that Mn_3O_4 is responsible for the NOx reduction is "Catalytic decomposition of NOx by Mn_3O_4 is known to be too slow to be practical at the NOx levels found in automotive exhaust." Ethyl's explanation for the NOx reduction is supported, however, by a Japanese patent abstract[24] which states "The title active catalyst consists of a monolithic catalyst support coated with an activated Al_2O_3 contg. Co [cobalt] oxide and Mn oxide ...". This particular invention showed the following automobile exhaust conversion:

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[23]GM's In-use Emission Performance Past, Present, Future, SAE Paper 881682.

[24]Exhaust Gas Treatment Catalyst Containing Cobalt and Manganese Oxides, Japanese Patent 63185453, August 1, 1988.

Co-Catalyst	Catalyst	Pollutant Conversion % HC	CO	NOx
Mn, Co, Al	Pt, Rh	60	92	98
Al	Pt, Rh	24	79	65

This result shows that combinations of Mn_3O_4 can affect improvements of NOx conversion (in this case 33 percent better). In a second Japanese patent[25], manganese is claimed as one of a list of metallic salts (which would be reduced to the oxide during calcining) that promote increased NOx removal. A third Japanese patent[26] also claims Manganese as a catalytic agent exhibiting enhanced NOx removal.

Ethyl's waiver request included a report from Dr. Roy Harrison which stated that the reaction temperatures and residence times in automobile exhaust systems were of the right order of magnitude to convert NOx. This information, together with the patent information noted above, clearly shows that the catalytic properties of Mn_3O_4 plausibly explains the reduction in NOx emissions observed in the Ethyl test program.

VI. Chrysler Comments on Catalyst Plugging

Relying on very limited and only partially documented information from current catalytic converters and pre-1981 SAE papers, Chrysler claims the use of HiTEC 3000 will cause catalyst plugging. Chrysler quotes SAE Papers 770655 and 780004 as relevant to catalyst plugging. As noted in response to Ford's comments, these studies were conducted on vehicles with outdated emission control systems, and at a dosage level for the additive up to 400% greater than that under consideration.

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[25] Automobile Exhaust Gas Purging Catalyst, Japanese Patent 58119343, July 15, 1983.

[26] Automobile Exhaust Gas Purging Catalyst, Japanese Patent 59139939, August 11, 1984.

Chrysler Canada provided Ethyl with several used catalysts removed from customer cars. These units were removed by the dealer service organizations for either noise or driveability problems if the dealer felt these units might be affecting driveability. All but a few of the catalysts were intact. These intact units would be expected to function properly and could not have been the cause of the "driveability" problem. All of the intact units have a dust coating of manganese oxide which would be expected. The amount of manganese coating varies, and differences may be due to the type of owner driving. None of these units would be considered to be "plugged." A few of the catalysts had broken or melted monoliths indicating excessive thermal stress. Manganese analysis was made on several of the units. In general the first inch of catalyst contained 1 - 5% manganese. Ethyl believes that this may be a normal range of manganese deposits for catalysts operated on the level of manganese found in Canadian gasoline.

In the Ethyl waiver submission, data are presented for a pair of close-coupled Ford Crown Victorias operated under high-speed conditions. This test was conducted to specifically address automobile industry concerns for catalyst plugging. Back pressure data on both cars remained constant at 8 psi indicating no catalyst plugging.

Chrysler submitted a quotation from the Johnson-Matthey paper, "the Effect of Fuel and Oil Additives on Automobile Catalysts."[27] The authors of that paper state that MMT is not expected to be used in European fuel due to adverse effects on catalysts and its toxicity in the environment. This statement is made in the absence of any of their own data and without any references to articles associated with environmental issues. In the body of the paper the authors acknowledge:

> "Data generated during the Coordinating Research Council's MMT Field Test Program showed no occurrence of catalyst plugging." and
>
> "A field test undertaken by Environment Canada has shown that 1983-85 model year cars operating on unleaded petrol containing MMT will meet the 1988 Canadian emissions standard of 0.41 g/mile hydrocarbon."[28]

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[27]See Chrysler submission, p. 2.

[28]The Effect of Fuel and Oil Additives on Automobile Catalyst Performance, Johnson-Matthey Platinum Metals Review, Vol. 34, No. 1, January 1990.

The study referred to in Ethyl of Canada's 1978 report, like other studies of the period, was conducted under "severe duty" engine dynamometer testing at high manganese concentrations and did not reflect current experience as shown in Ethyl's waiver application.

The Ford reference (SAE 890582) cited by Chrysler has previously been reviewed in this Appendix.

The selective data cited by Chrysler, therefore, does not refute the results of Ethyl's test program -- i.e., that HiTEC 3000 does not cause catalyst plugging at the concentration level requested in this waiver application.

VII. Chrysler Comments on HC Emissions

With respect to the Additive's impact on HC emissions, Chrysler refers to several publications from 1977.[29] As discussed earlier, data on vehicles from that period are not relevant to this waiver request. Since 1977, catalyst and automotive technology have improved significantly, resulting in major reductions in tailpipe emissions. Further, much of the earlier data were obtained at manganese concentrations that are 200% to 400% higher than the concentration requested in the current waiver. Thus, conclusions regarding HC emissions that are drawn from the 1977 CRC data will not be valid for current production vehicles.

Similarly, data from SAE paper 770655 and CARB staff Report 77-9-3 are based on operating 1977 automobiles using fuel containing high manganese concentrations.

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[29]Chrysler Corporation Technical Response to Environmental Protection Agency, July 20, 1990, p. 5.

While it is important in any scientific investigation to review all existing data, it is necessary to put older data into proper context. The data from 1977 have been superceded by Ethyl's current fleet study. Ethyl's data on current model cars demonstrate that tailpipe hydrocarbon emissions from fuels containing 0.03125 gm Mn/gallon as HiTEC 3000 are nearly as low as from clear fuels.

Chrysler contends that this small difference in hydrocarbon emissions, 0.010 to 0.018 gm/mile, will present greater problems in the future when the HC emission standard is lowered to 0.25 gm/mile. As engine and emission control technology improves, it is realistic to assume that catalyst conversion efficiency also will rise, similar to that exhibited when one compares conversion efficiency data from the 1978 CRC test program to that generated by the Ethyl test program (i.e. an increase in average conversion efficiency from 77 to 85.9 percent. The small HC difference found in the current program could be reduced even more by future emission technology.

As previously discussed, Environment Canada studied the effect of HiTEC 3000 on vehicle emission systems. The working group from CGSB, which contained representatives from the Motor Vehicle Manufacturers' Association and the Automotive Importers of Canada, supported the continued use of HITEC 3000 (MMT) as an octane enhancer. Additionally, MVMA and AIC indicated that warranty claims were no higher in Canada than in the U.S. where manganese was not used in unleaded gasoline.

VIII. U.S. Catalyst Inspections

Neither Ford nor Chrysler presented any data comparing catalyst converter durability in Canada to similar data in the U.S. to support their claims. Consequently, Ethyl conducted an informal survey of vehicle maintenance firms in Baton Rouge, Louisiana. The comments from these firms indicate that converter replacements are not uncommon in the U.S. In fact, the automobile industry acknowledged in the CGSB report that warranty claims occur about as often in the U.S. as in Canada.[30]

The catalysts shown in Attachment 5 were removed from automobiles in consumer service by a muffler shop in Baton Rouge, Louisiana. The 40 catalysts collected from this shop, which has three outlets in Baton Rouge, were removed during period of approximately one month during 1990, from cars which had been driven more than 50,000 miles. No data on mileage, fueling, or specific malfunction was collected. The catalysts were removed because of malfunctions which were diagnosed (by the owner and/or the muffler shop, or another auto repair shop) as indicating problems with the catalyst. Typically, the car would not accelerate as it should and/or had lost the ability to operate at a reasonable speed.

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[30] Canadian General Standards Board Report, April 1986.

Photographs of the catalytic converters are an inadequate substitute for the data generated from a controlled test program, nevertheless, they can illustrate the existence of problems in the U.S. as seen in the photographs of seven (7) of these catalysts. Photo #1 appears to be normal, Photos #3, 4 and 5 indicate various levels of plugging while Photos #2, 6 and 7 indicate varying levels of over temperature operation. These catalysts along with another 33 catalysts were selected at random. This information further confirms that the Additive does not cause catalyst plugging.

As previously mentioned, the lack of routine maintenance, misfueling, excessive oil consumption, and engine misfiring can and do cause catalyst problems. The use of the Additive does not.

IX. Conclusion

All automotive company commentators relied predominantly on research studies conducted over a decade ago on vehicles equipped with outdated emission control technology to support their concern/opposition to Ethyl's waiver application. Neither Ford nor Chrysler (who submitted most of the information) attempts to dispute directly the test results reported by Ethyl in support of its waiver application. For the reasons noted above, the studies cited by Ford and Chrysler do not refute the results of Ethyl's extensive test program. The Agency should, therefore, grant Ethyl's waiver application.

ATTACHMENT 1

ETHYL CORPORATION

INTER-OFFICE

TO:	Kevin L. Fast	ADDRESS:	FAX 202/778-2201
FROM:	Ben F. Fort	ADDRESS:	BRT-6
SUBJECT:	Louisiana State Police Experience with Catalyst Replacement	DATE:	August 7, 1990

The severity of service for police vehicles is much higher than ordinary vehicle usage. In our search for examples of catalyst failure, the Louisiana State Police were contacted to determine their experience with catalyst failure.

The first contact was on June 7, 1990 with a state trooper in the research group who described several instances of exhaust system failure on cars driven 40,000 to 60,000 miles. Some of the failures were mufflers and some were catalysts. He suggested that I contact the maintenance group for additional information.

The maintenance contact told me that about nine months ago almost 400 cars with high mileage (about 60,000 to 80,000 miles) were decommissioned and sold. Unfortunately, the maintenance records are discarded when vehicles are sold. However, he related that most of those cars were '85 and '86 models, and they were replacing catalysts "right and left" after 30,000 to 40,000 miles of service. The state police use a local muffler shop to replace catalysts. A replacement program was discussed to secure police car catalysts for examination. Contact with the muffler shop revealed that catalysts are replaced frequently and not just on police vehicles. In fact, they had a "stockpile" of used catalysts currently available. The ready availability of catalysts led us to abandon the plan for additional police vehicle catalysts to concentrate on the readily available replaced catalysts. The maintenance records from the state police are available for future use and will show surprisingly high catalyst replacement rates for the new fleet now in service.

Sincerely,

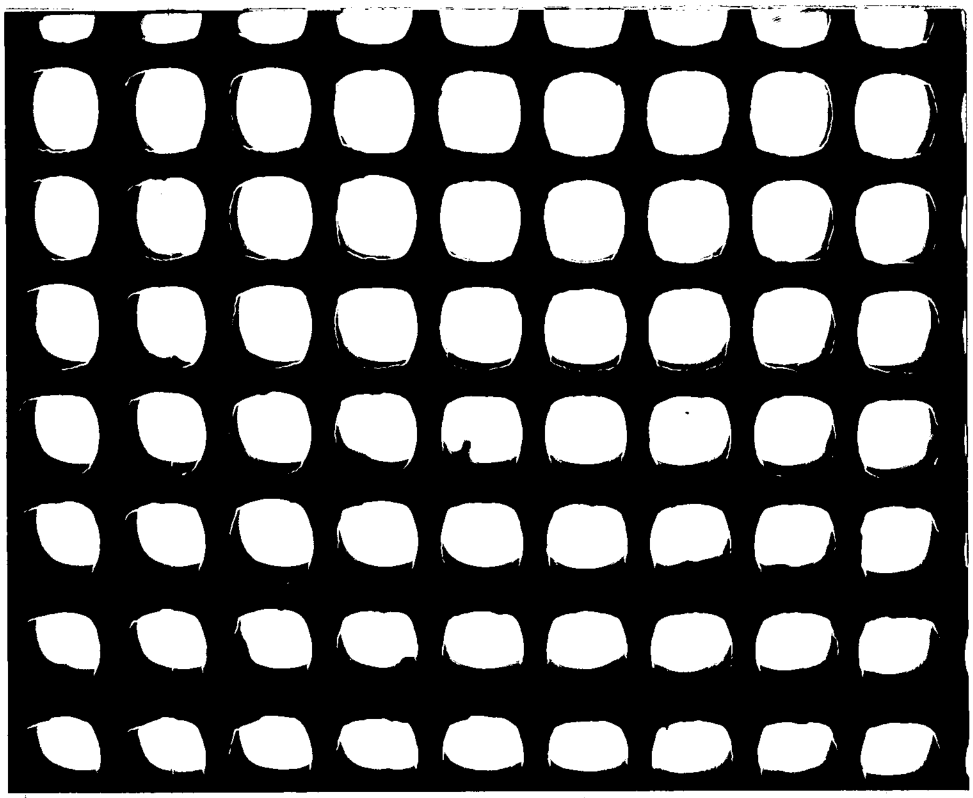
Ben F. Fort, Jr.

Ben F. Fort, Jr., Ph.D.
Senior Mathematics
and Statistical Associate

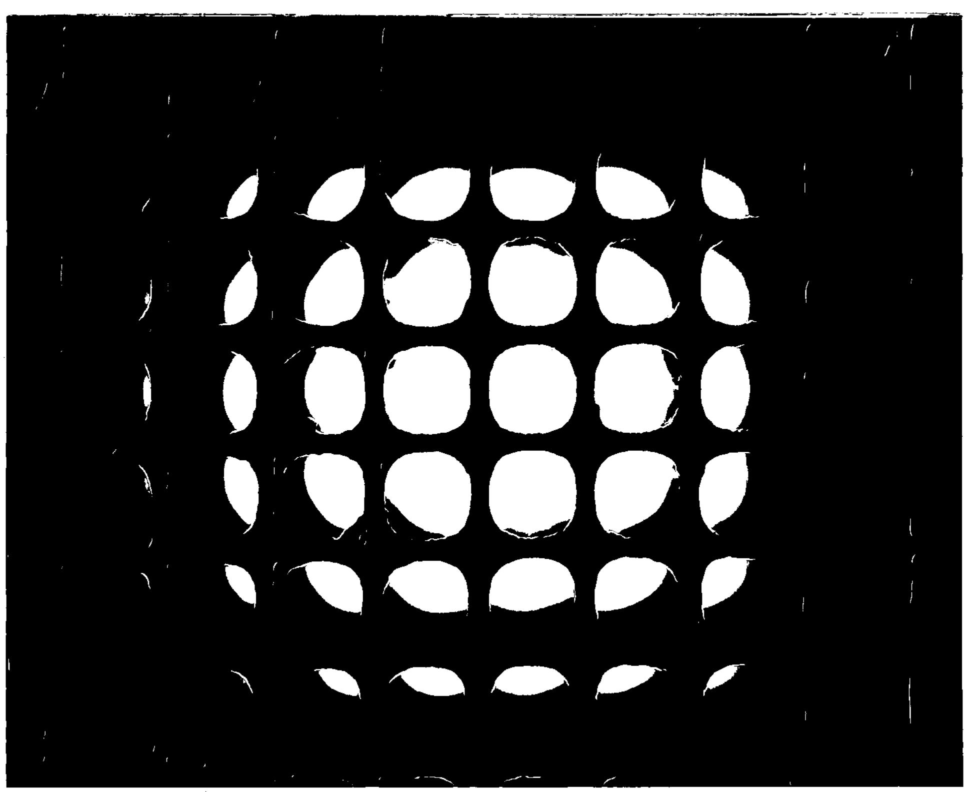
BFF:cr
021BFF90

ATTACHMENT 2

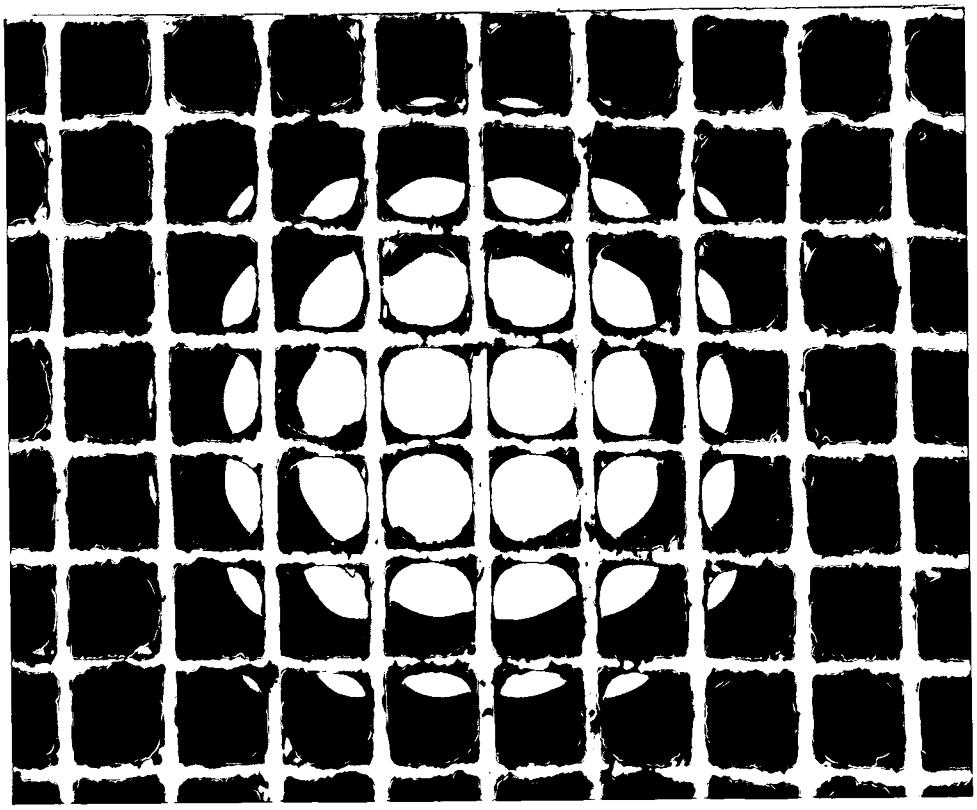
1986 3.0L Ford Taurus
102,000 miles
Inlet Face, first 1/2"



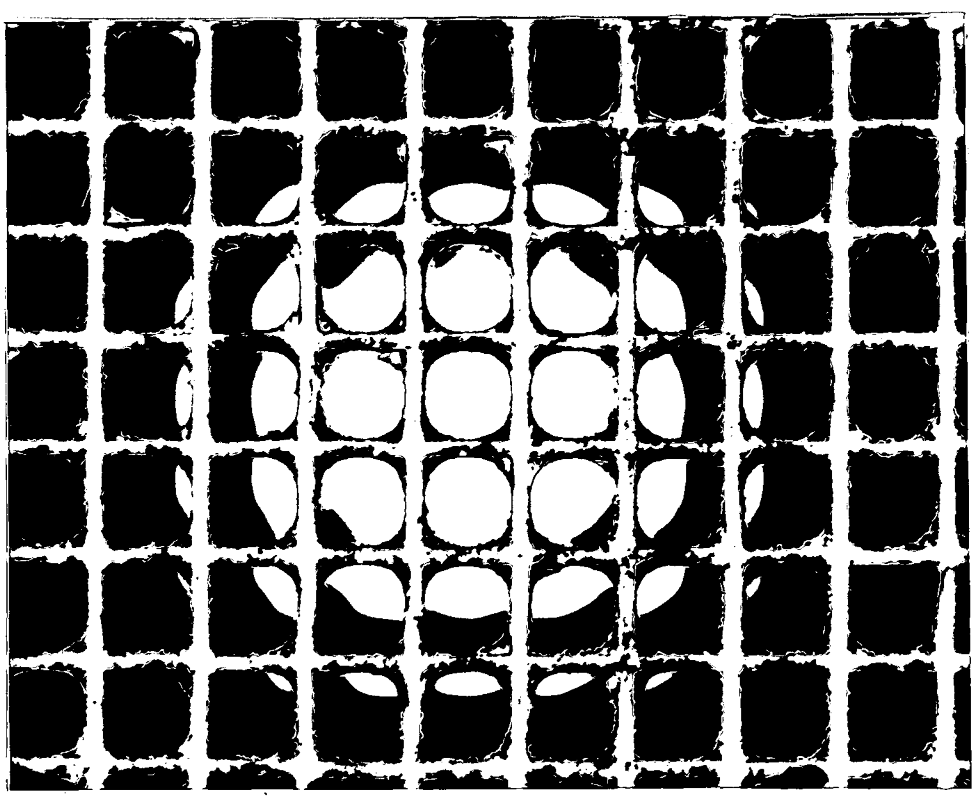
1986 3.0L Ford Taurus
102,000 miles
Inlet, second 1-1/2"



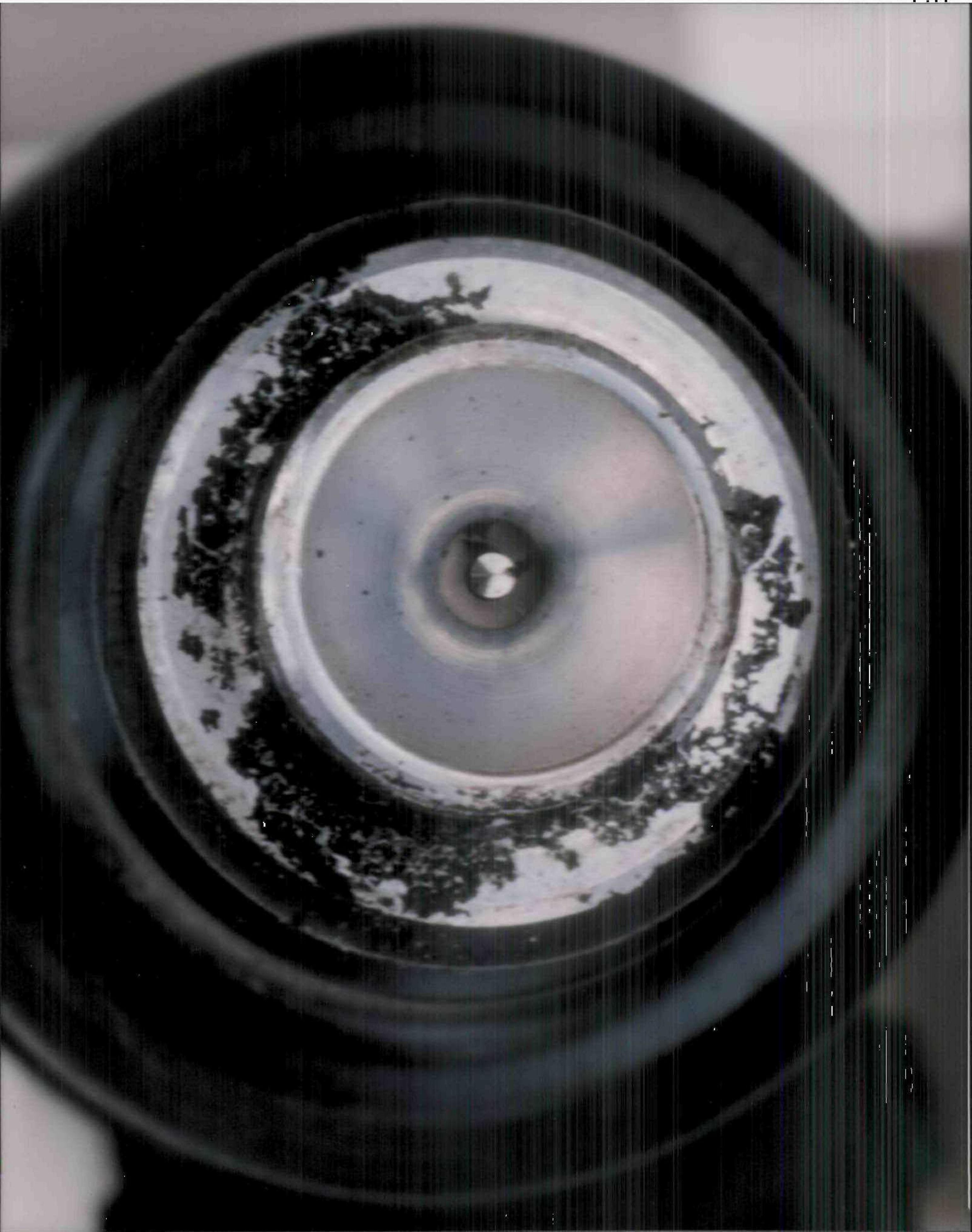
1986 3.0L Ford Taurus
102,000 miles
Middle, 1-1/2″



1986 3.0L Ford Taurus
102,000 miles
Rear, 1-1/2″



ATTACHMENT 3

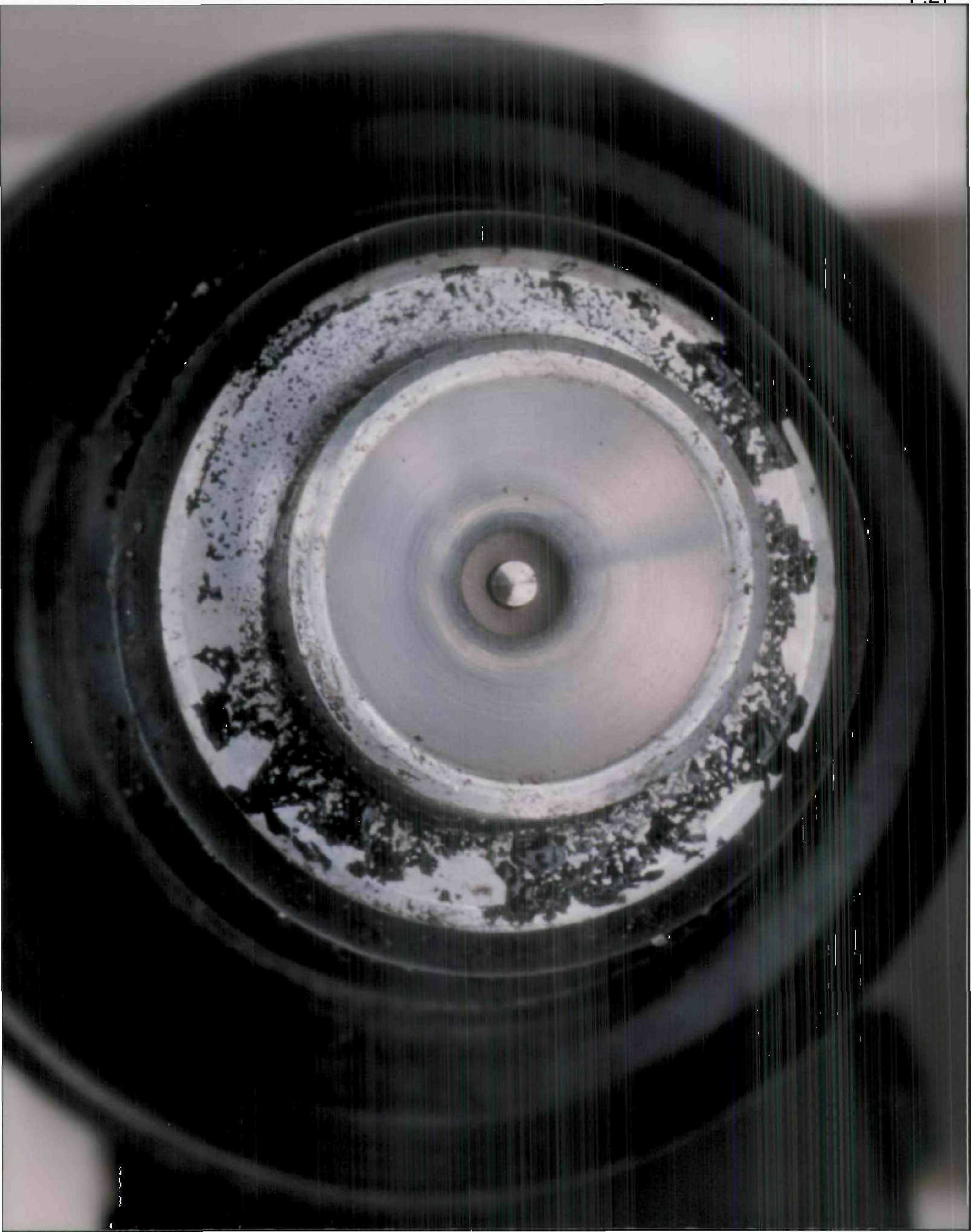


R1F10

FOR FUTURE ORDERS PLEASE REFER TO:
Commercial ETHYL
Industrial Images JOB#:4414
P.O. Box 2468 ROLL#:1
Baton Rouge, LA 70821 FRAME#:10
(504) 768-7343 DATE:8/1/90
FUEL INJECTOR D350K #1

CAR D-3
FUEL INJECTOR #1
50,000 MILES

CAR D-3
FUEL INJECTOR #2
50,000 MILES



FOR FUTURE ORDERS PLEASE REFER TO:
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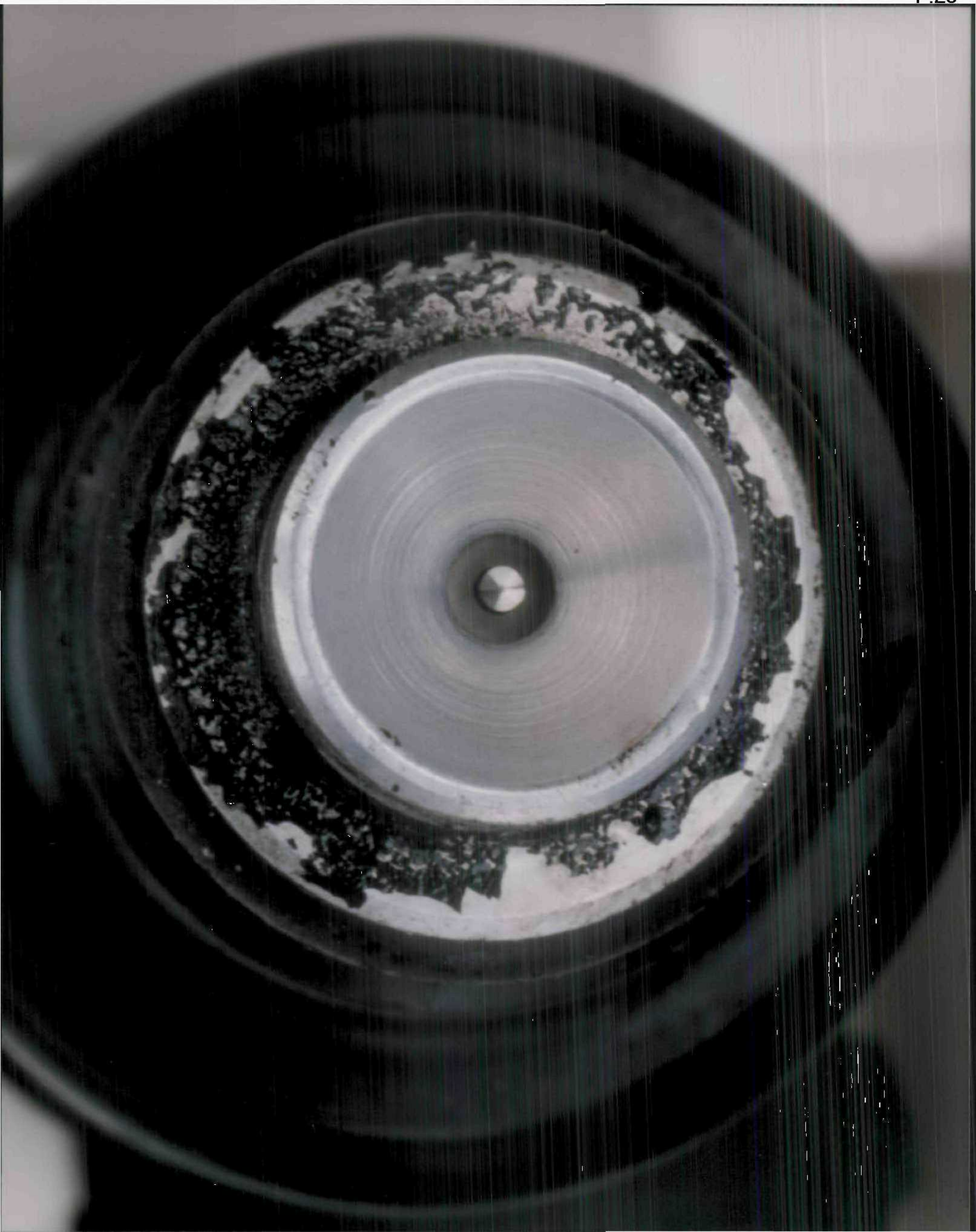
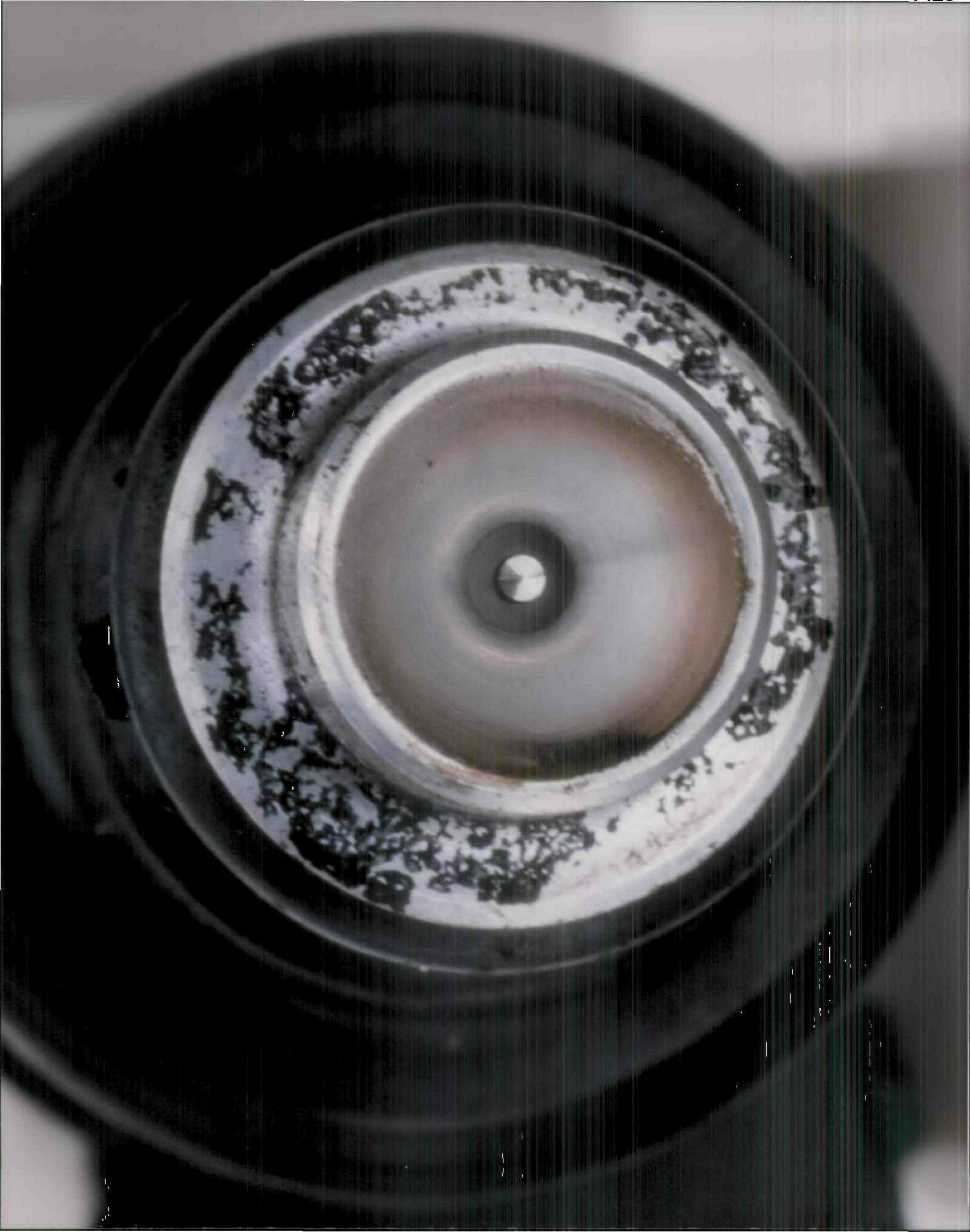
Industrial Images JOB#:4414
P.O. Box 2468 ROLL#:1
Baton Rouge, LA 70821 FRAME#:15
(504) 768-7343 DATE:8/1/90
FUEL INJECTOR D350K #2

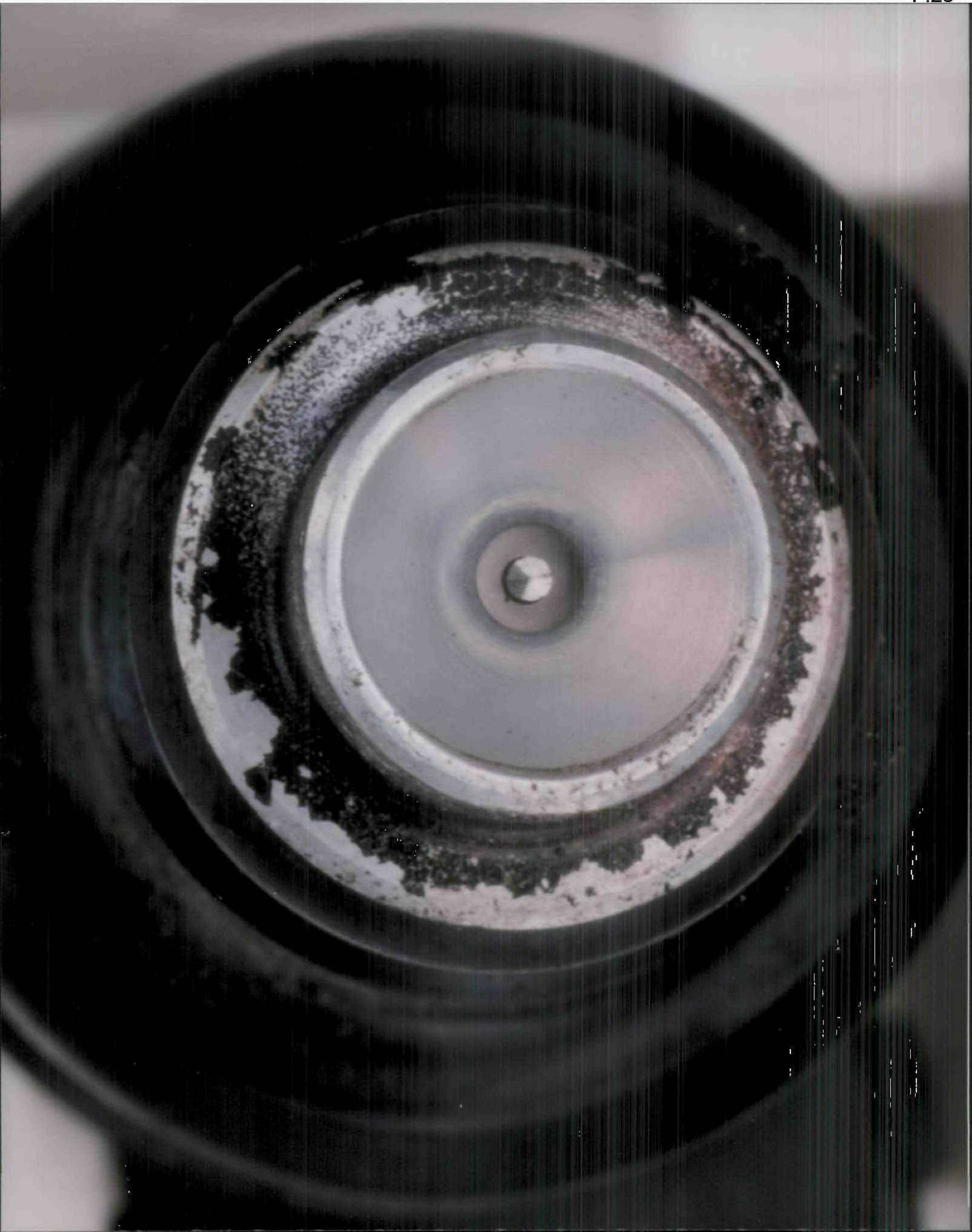
12/15/5

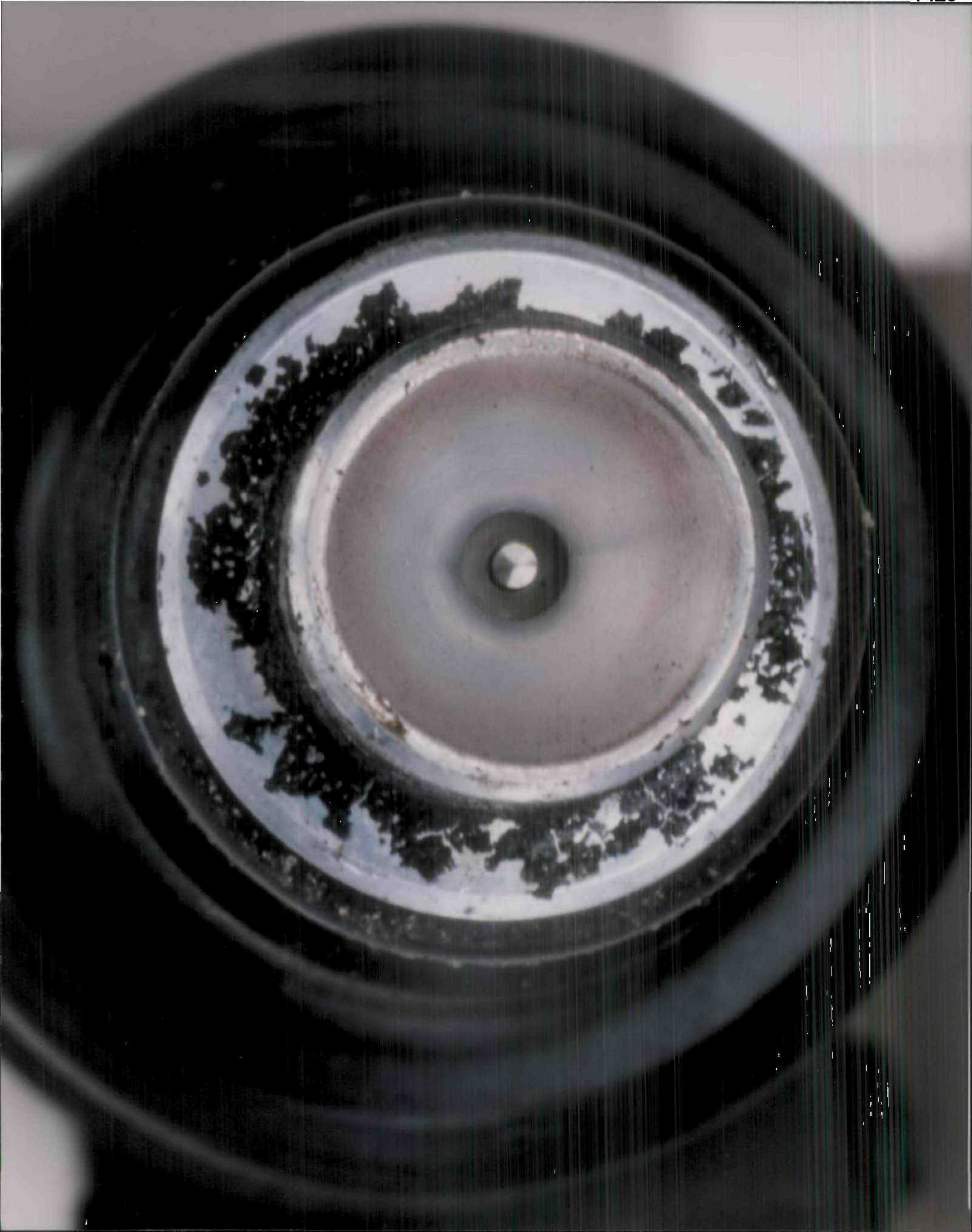


Car D-3
Fuel Injector #3
50,000 miles



Car D-3
Fuel Injector #5
50,000 miles





FOR FUTURE ORDERS PLEASE REFER TO:

Commercial ETHYL

Industrial Images JOB#:4414

P.O. Box 2468 ROLL#:2

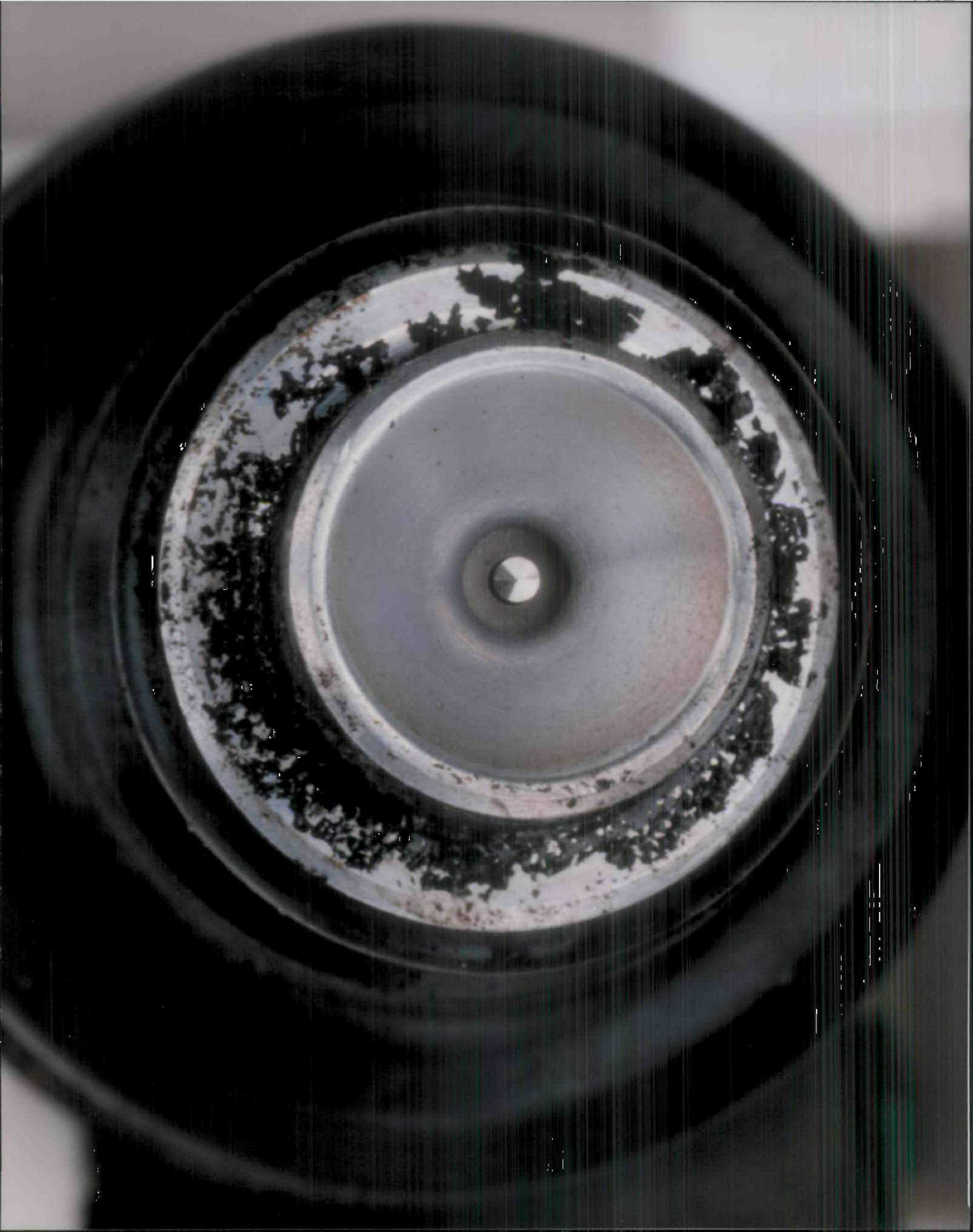
Baton Rouge, LA 70821 FRAME#:7

(504) 768-7343 DATE:8/1/90

FUEL INJECTOR D450K #1

2/22

CAR D-4
FUEL INJECTOR #1
50,000 MILES



R2F/2

FOR FUTURE ORDERS PLEASE REFER TO:
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Industrial Images   JOB#:4414
P.O. Box 2468   ROLL#:2
Baton Rouge, LA 70821 FRAME#:12
(504) 768-7343   DATE:8/1/90
FUEL INJECTOR D450K #2

FOR FUTURE ORDERS PLEASE REFER TO:
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Industrial Images JOB#:4414
P.O. Box 2468 ROLL#:2
Baton Rouge, LA 70821 FRAME#:14
(504) 768-7343 DATE:8/1/90
FUEL INJECTOR D450K #3

12294

Car D-4
Fuel Injector #3
50,000 miles

FOR FUTURE ORDERS PLEASE REFER TO:
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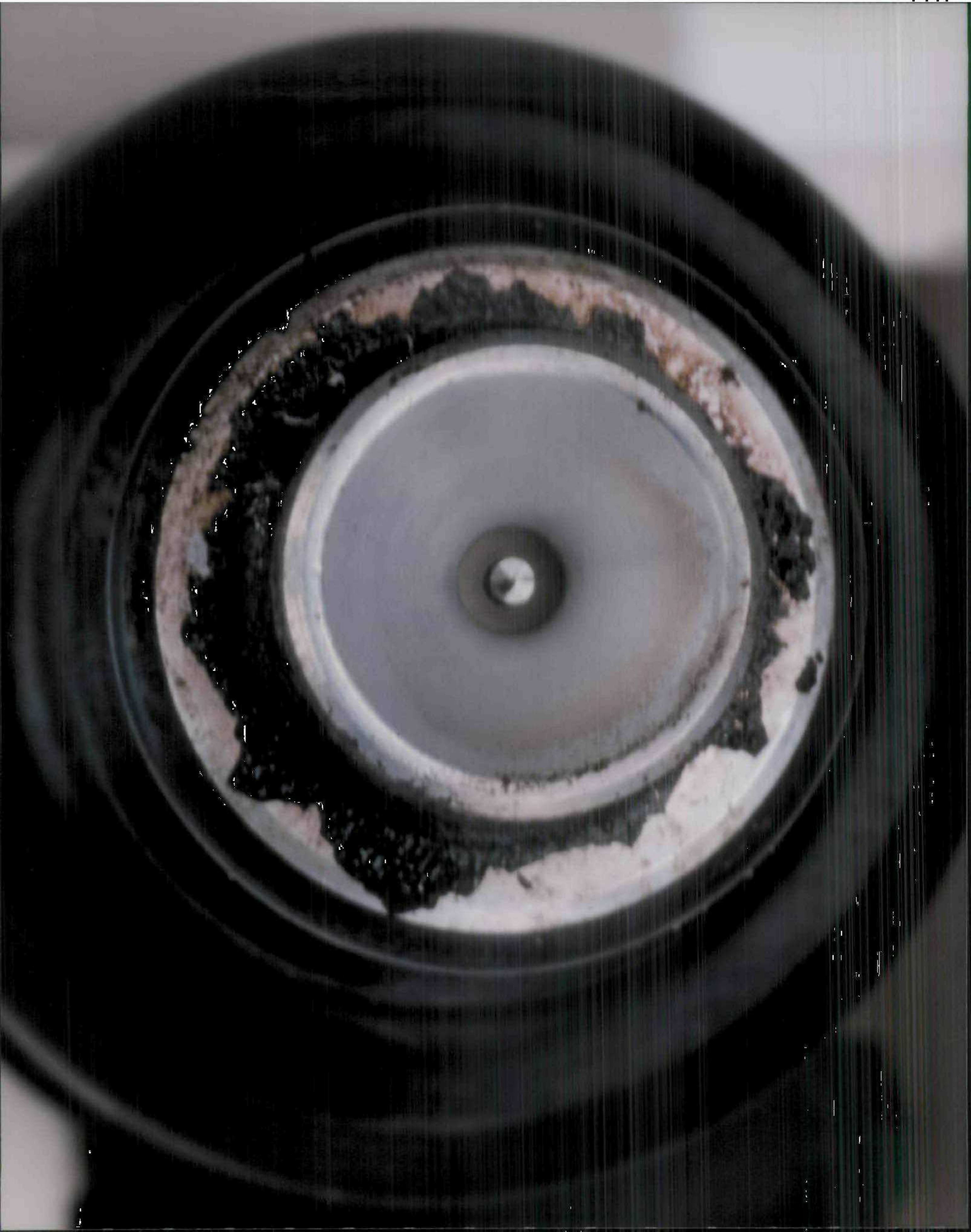
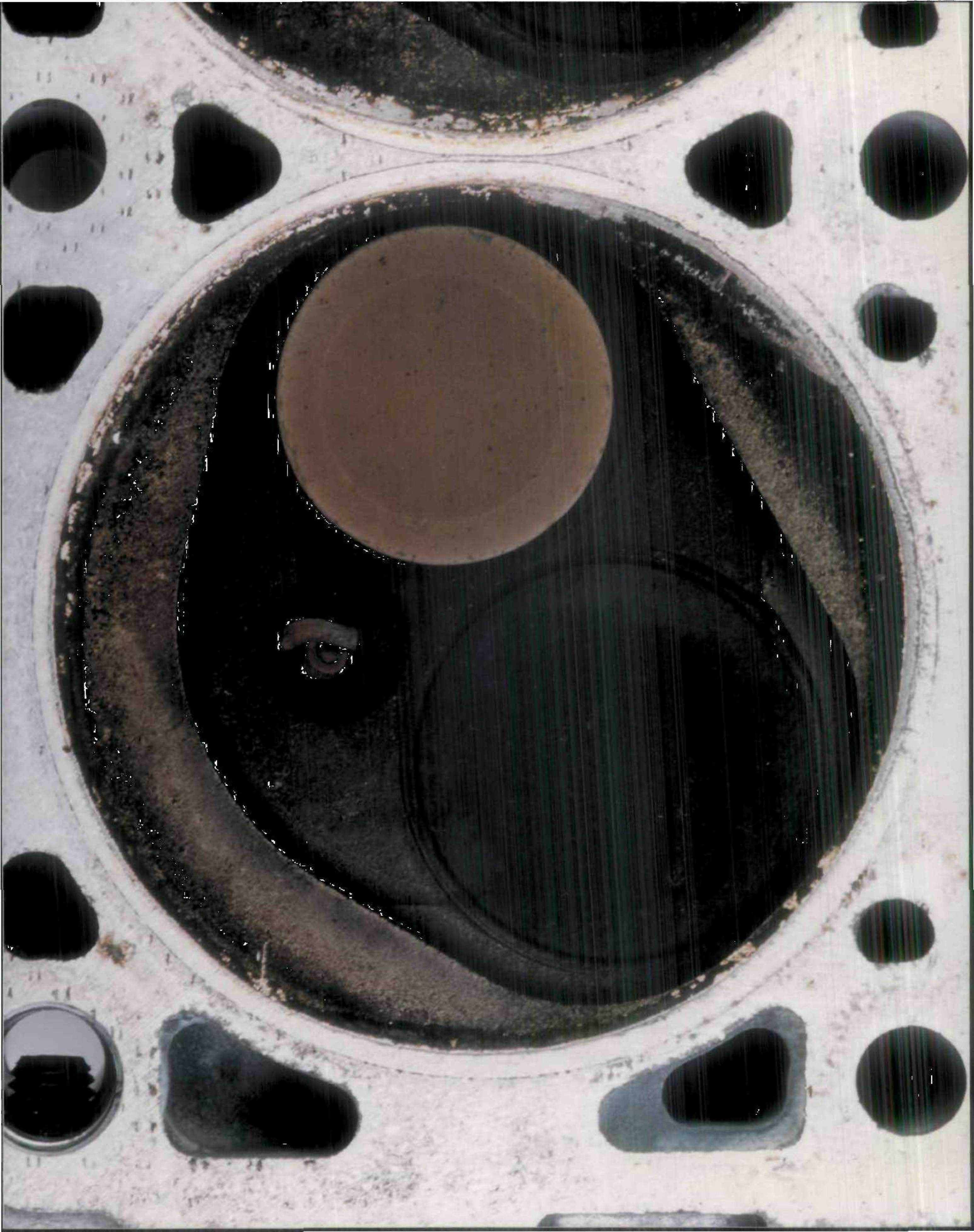
Industrial Images JOB#:4414
P.O. Box 2468 ROLL#:2
Baton Rouge, LA 70821 FRAME#:15
(504) 768-7343 DATE:8/1/90
FUEL INJECTOR D450K #4

122E/15

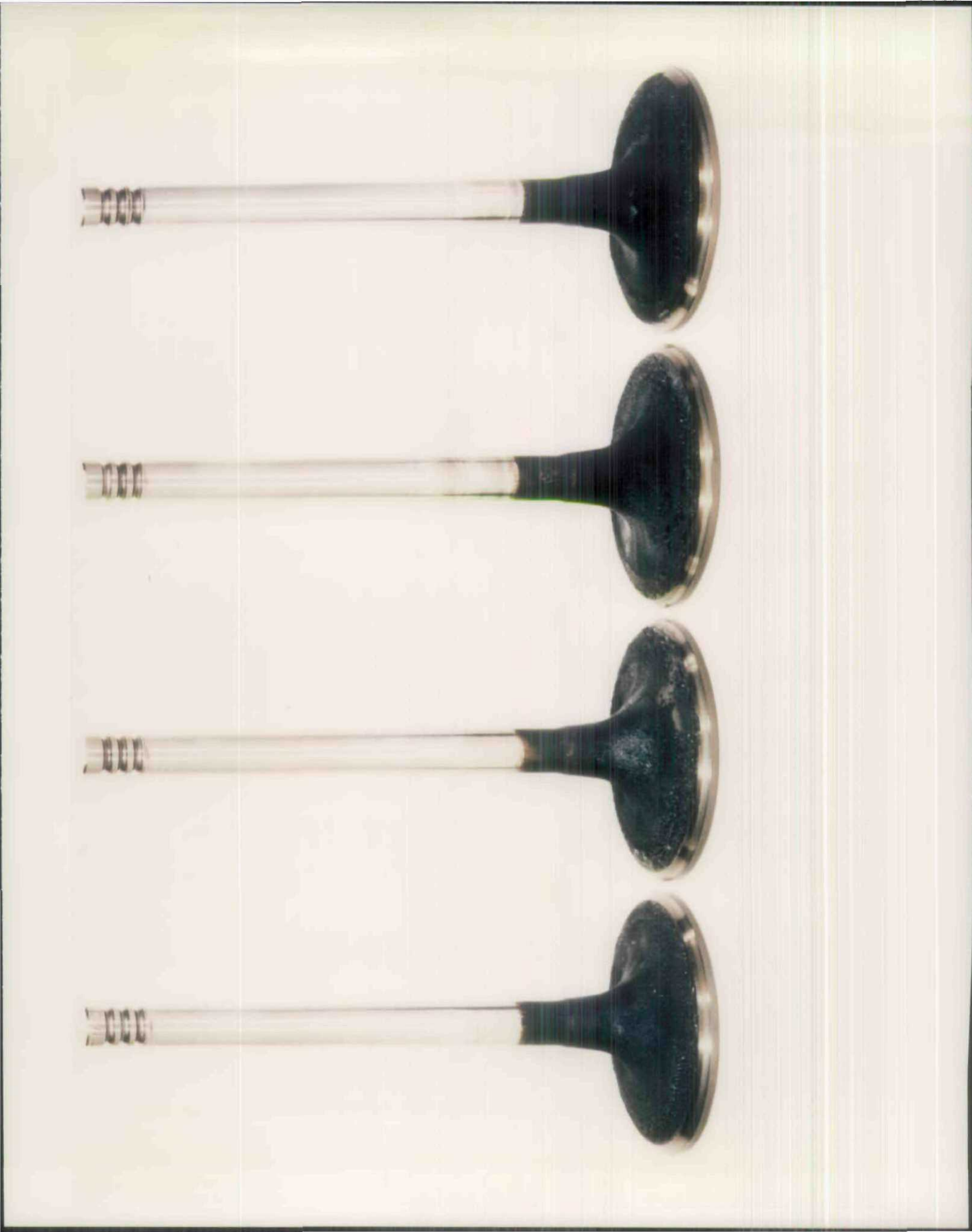
CAR D-4
FUEL INJECTOR #5
50,000 MILES



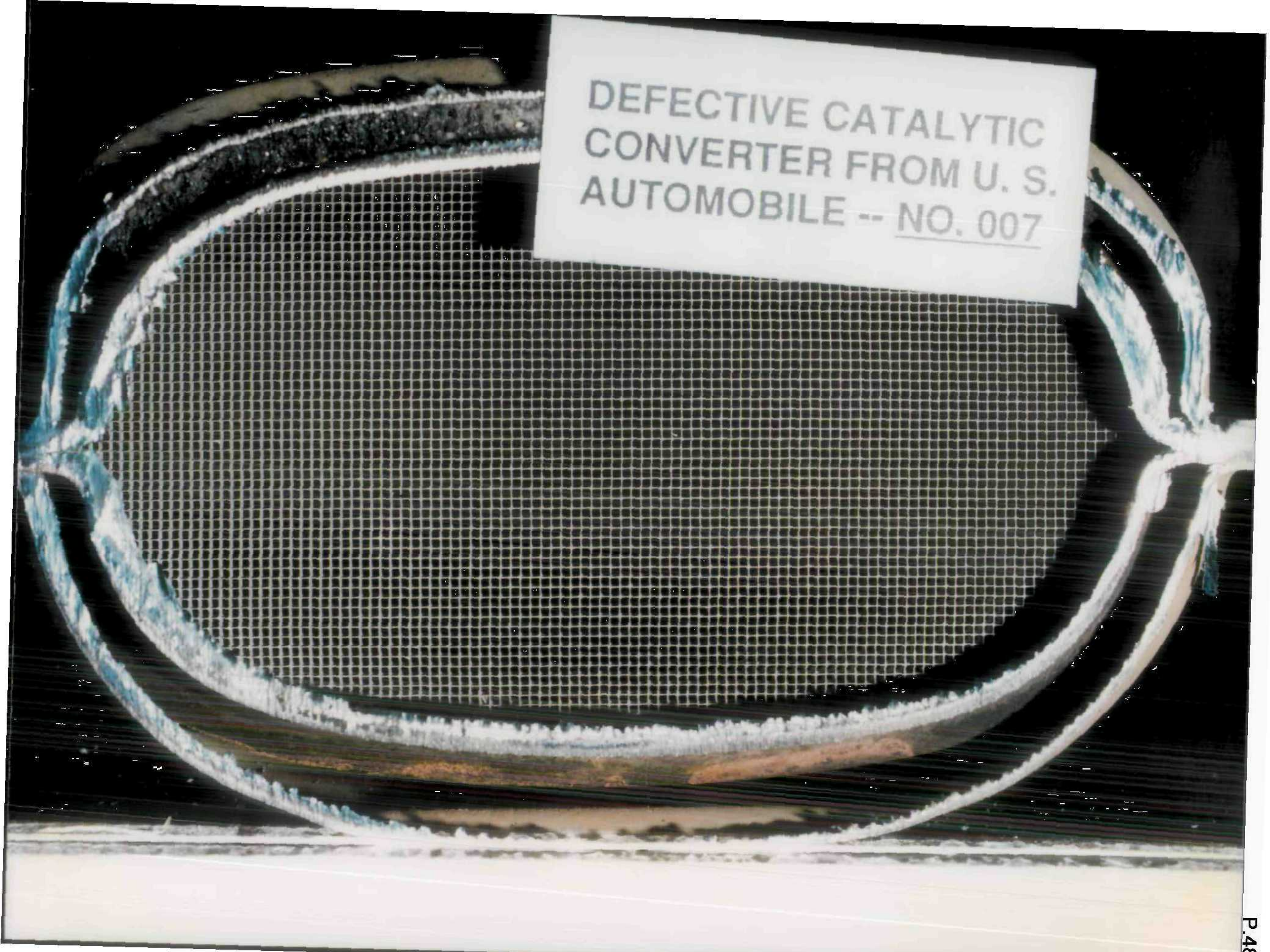


Car C-6
Cylinder Head


DEFECTIVE CATALYTIC
CONVERTER FROM U. S.
AUTOMOBILE -- NO. 012



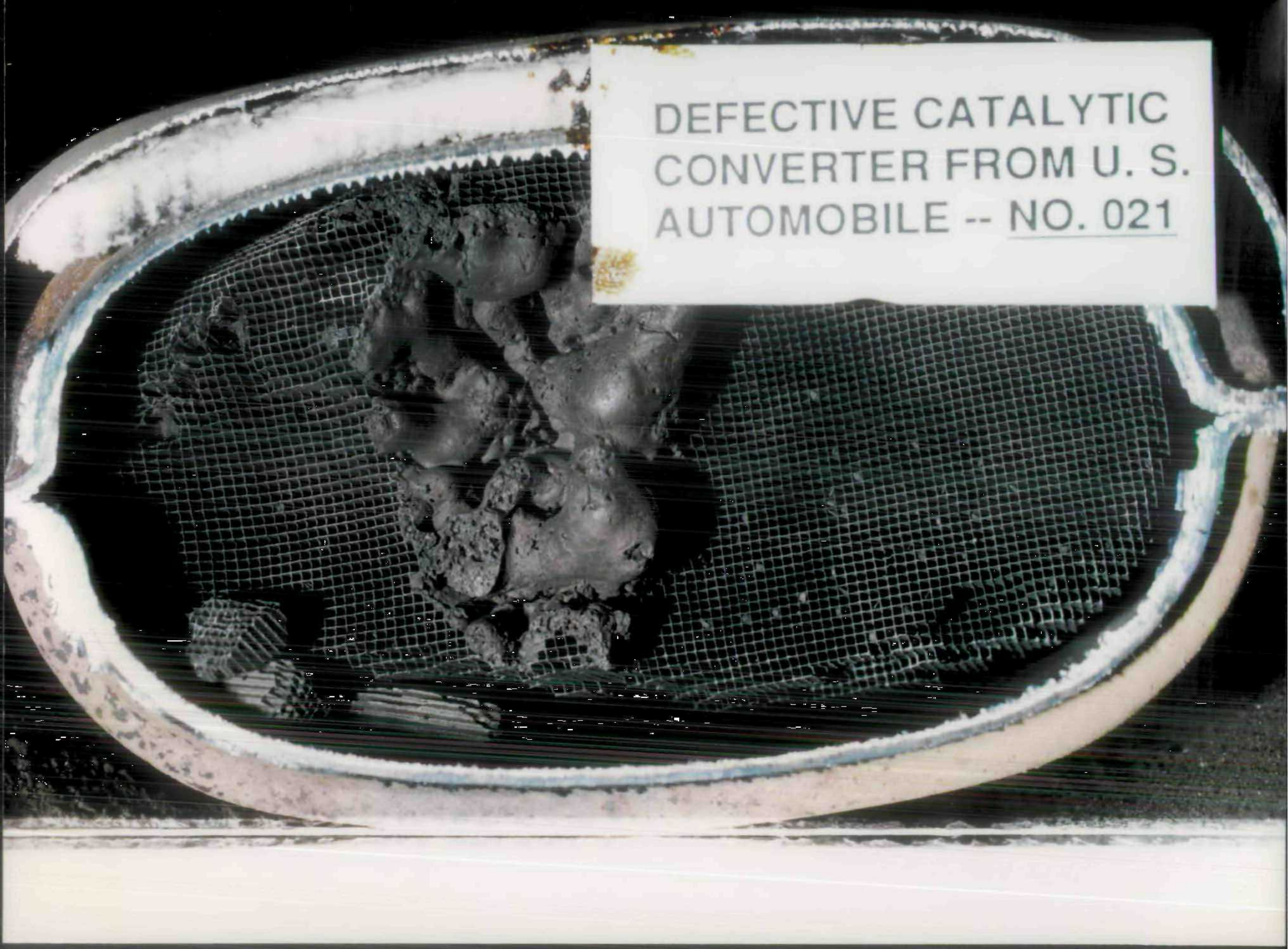
COMMERCIAL GASOLINE
INTAKE VALVES


DEFECTIVE CATALYTIC
CONVERTER FROM U. S.
AUTOMOBILE -- NO. 007


DEFECTIVE CATALYTIC
CONVERTER FROM U. S.
AUTOMOBILE -- NO. 018


DEFECTIVE CATALYTIC
CONVERTER FROM U. S.
AUTOMOBILE -- NO. 019


DEFECTIVE CATALYTIC
CONVERTER FROM U. S.
AUTOMOBILE -- NO. 023


DEFECTIVE CATALYTIC
CONVERTER FROM U. S.
AUTOMOBILE -- NO. 021


DEFECTIVE CATALYTIC
CONVERTER FROM U. S.
AUTOMOBILE -- NO. 015

3

Aigner L INDEX™ · EXHIBIT DIVIDERS

3

TO: Ethyl Corporation

FROM: Systems Applications, Inc.

SUBJECT: Analysis of Ford's Submittal to the EPA, Attachment 5

DATE: 9 August 1990

In response to Ethyl Corporation's HiTEC 3000 waiver application, comments were received by the EPA from Ford Motor Company. These comments, dated 23 July 1990, represent Ford's review of Ethyl's waiver request and detail, in part, Ford's findings in regards to the effects of HiTEC 3000 on vehicle emissions and emission control systems.

Of particular interest is Attachment 5 of the Ford submittal. In this attachment, Ford provides results of their analysis of the percent effect of HiTEC 3000 (MMT) over baseline, an evaluation of the effect of HiTEC 3000 on engine-out and tailpipe emissions at 50K and 75K, a plot of the percent difference between Ethyl's baseline data and Ford's certification emission data, and finally, a graphical analysis of the effects of HiTEC 3000 on vehicle emissions by vehicle group. Ford states as a note on the cover of Attachment 5 that the figures and tables contained in their report were derived from test data provided by Ethyl. It is assumed from this note that the data set analyzed by Ford was ETHYL4S2, the main data set used in the statistical work performed by Systems Applications.

The purpose of this memorandum is twofold. First, this memo provides an evaluation of the analysis conducted by Ford as contained in Attachment 5 of their submittal to the EPA in response to Ethyl's HiTEC 3000 waiver application. In an attempt to confirm Ford's reported results, efforts were made to duplicate the procedures used by Ford in their analysis. Second, to address the questions raised by Ford in their submittal regarding the effect of HiTEC 3000 on catalyst converter performance, an evaluation of the statistical significance of the conversion efficiencies of all vehicle model groups (with the exception of vehicle group F) was also performed. The results of both analyses are summarized below.

Evaluation of Ford's analysis

To evaluate the results reported by Ford, Table 1 (Percent effect of HiTEC 3000 over baseline) and Figures 4 through 27 (Effects of HiTEC 3000 on vehicle emissions by vehicle group) were compared with the data in ETHYL4S2. Although in general our evaluation of the table and figures confirmed the results reported in the Attachment, significant errors in Ford's analysis of vehicle groups C and H were encountered. In addition, the results reported for vehicle groups H and I in Table 1 have apparently been switched by Ford. Furthermore, small errors in Table 1 results for vehicle group H exist. As a note, Figures 1 through 3 were not evaluated because of the unavailability of Ford's certification emissions data.

<u>Figures 4 through 27</u>

Specific analysis of Figures 4 through 6 (vehicle group C) show completely inaccurate results when compared with ETHYL4S2. This is particularly true for NOx. When compared with the mean emission effects reported in Table 1, it can be seen that the NOx percent effect averaged over range is smaller (greater negative value) than every value reported in Figure 6; in fact all percentage differences in Figure 6 should be negative. This is confirmed by the plotted results shown in Attachment 2A of Ethyl's waiver application (p. B-55).

Ethyl Corporation
9 August 1990
page 3

In addition to the inaccuracies shown for vehicle group C, small errors in the reported results for vehicle group H (Figures 19 to 21) also exist. These errors relate to the results shown for the intervals at 30K and 35K miles. In Ford's analysis, the NOx effect at 30K and 35K are reported to be 15 and 5 percent respectively. In actuality, the data contained in ETHYL4S2 shows the actual effect to be 6 percent at 30K and 17.5 percent at 35K.

Table 1

The reported results contained in Table 1 of Ford's Attachment 5 were also evaluated by comparison to ETHYL4S2. From this evaluation, it is clear that the results shown for vehicle groups H and I are switched. In addition, small errors in the results for vehicle group H exist. No other discrepancies between results reported by Ford and those calculated by Systems Applications for this evaluation were encountered.

One additional point should be made about the results detailed by Ford in Table 1. At the bottom of this table, Ford's shows a calculated average percent difference in the effect of HiTEC 3000 over baseline. From our evaluation, it appears that this is an unweighted average. Because of Ford's use of an unweighted average percent effect, the results shown give a slightly distorted view of the effect of HiTEC 3000. By taking an unweighted average, Ford suggests that it is appropriate to assume that all vehicle groups in the fleet program are represented equally in the national fleet. As can be seen in Attachment 2A of Ethyl's waiver application (p. 5), this is clearly not the case. It is therefore more appropriate to evaluate the effect of HiTEC 3000 on a weighted average basis as was done in the waiver application.

On the attached, we have provided a revised Table 1 showing the correct results for vehicle groups H and I. In addition, we have calculated and shown the percent effect of HiTEC 3000 over baseline on a weighted average basis.

Engine out analysis

Using a similar approach to the methodology used to evaluate Ford's analysis in Table 1 and Figures 4 through 27, the results shown in Table 2 were also compared with data from ETHYL4S2. In our evaluation of Table 2, we were unable to reproduce any of the results shown by Ford. The results provided in the table are quite inconsistent with the data in ETHYL4S2 and with Ford's Figures 10 through 12 and 25 through 27 (vehicle groups E and T respectively). The values for 50,000 mile engine-out emissions depend on how the multiple observations for each vehicle are averaged. The methods used by Ford were unknown to us and may offer some explanation for the difficulties we encountered in obtaining duplicate values.

In addition to analyzing Ford's Table 2, an additional analysis on engine-out and tailpipe emissions for each vehicle (except D3) was performed. This analysis involved the calculation of conversion efficiencies. The conversion efficiency at a given mileage was defined as 1 minus the ratio of average tailpipe to average engine-out emissions. To determine the average tailpipe emissions for each vehicle, we used the averages from the ETHYL4S2 data (first two emissions tests only). For engine-out emissions, two or more tests were carried out at 50,000 miles (before and after the component changes). In addition, two tests were always carried out at 75,000 miles. No engine-out tests were performed on vehicle group F at 50,000 or 75,000 miles due to the coupling of the catalyst to the engine manifold preventing the insertion of an emission probe. No engine-out tests were performed on vehicle group

I at 75,000 miles. To be consistent with the decision to omit 50,000 mile post-component change tailpipe emissions tests for the main working data set, we chose to use only the first two engine out tests at 50,000 miles for computing average engine-out emissions.

The conversion efficiencies were computed for each vehicle and pollutant at 50,000 and 75,000 miles. Averages across vehicles for each model group and fuel combination are reported in the attached tables. In these tables we also report results of statistical tests evaluating whether the HiTEC 3000 effect is beneficial against the null hypothesis that there is no effect or an adverse effect. In these tests, a low significance level (below about five percent) is strong evidence that the effect of HiTEC 3000 is beneficial with regard to conversion efficiencies. The tests performed parallel the statistical approach used in analyzing the integrated emissions in the waiver application (Appendix 2A, tables D-22 to D-24) with the exception that the integrated emissions for a vehicle were replaced by the conversion efficiency.

The overall results are as follows: For HC, there is no statistically significant effect at 50,000 miles (beneficial or adverse) but the effect at 75,000 miles is significantly beneficial (six percent level) using the most powerful weighted average test. For CO the reverse pattern appears: the effect is not significant at 75,000 miles but is significant (seven percent level) at 50,000 miles. For NO_x the effect is highly statistically significant at both mileages (two and zero percent levels). In each case the effect is either significantly beneficial or not adverse. There is no evidence of an adverse effect on conversion efficiencies.

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Table 1. Percent effect of MMT over baseline (averaged over range).

	Emissions (0 - 75K miles)			Emissions (0 - 50K miles)		
Model	HC	CO	NOx	HC	CO	NOx
C	21.44	8.77	-27.17	23.60	8.44	-22.32
D	5.62	-2.08	7.61	11.05	1.42	12.40
E	8.28	5.07	-7.11	14.04	12.58	-5.33
F	3.01	-34.61	-26.98	0.27	-29.94	-20.44
G	22.67	2.36	-4.69	23.16	-1.26	-1.62
H	2.34	-7.77	-0.82	-0.39	-9.42	13.04
I	5.79	-3.47	-15.75	4.90	-0.65	-7.78
T	8.51	-1.34	-28.12	12.41	4.79	-30.54
Unweighted Average % Dif.	9.71	-4.13	-12.88	11.13	-1.75	-7.82
Weighted Average % Dif.	8.17	-5.74	-13.78	8.53	-3.67	-7.34

Ethyl Corporation HiTEC 3000 Fleet Testing Program

50,000 Miles Conversion Efficiency Test
Pollutant Hydrocarbons

Model	Conversion Efficiency 50,000 miles			Rank Sum Test			T-test
	EEE	HT3	Sign	Test Statistic	Mean	Sig.Level (%)(b)	Sig.Level (%)(b)
D	0.765	0.720	-	4.0	3.0	80.00	82.23
E	0.873	0.891	+	2.0	4.5	20.00	13.22
T	0.830	0.851	+	1.0	4.5	10.00	3.53
C	0.888	0.877	-	7.0	4.5	90.00	83.28
G	0.896	0.893	-	6.0	4.5	80.00	59.75
H	0.896	0.894	-	5.0	4.5	65.00	55.73
I	0.906	0.919	+	0.0	4.5	5.00	6.54
Weighted Average(c)	0.879	0.883	+				26.13
Total				25.0	30.0	19.73	

EPA Sign Test: Observation of 3 '+' sign(s) in 7 trials rejects the hypothesis of no beneficial HiTEC 3000 effect at the 77.34 percent significance level(b).

EPA Overall Rank Sum Test: The hypothesis of no beneficial HiTEC 3000 effect is rejecte at the 19.73 percent significance level(b).

Weighted Average Test: The hypothesis of no beneficial HiTEC 3000 effect is rejected at the 26.13 percent significance level(b).

Notes:
a. Each figure is the mean of the conversion efficiencies at 50,000 miles for each fuel.
b. The lower the significance level, the greater the evidence of a beneficial HiTEC 3000 effect.
c. The weights for the weighted averages are proportional to 1988 sales figures.

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Ethyl Corporation HiTEC 3000 Fleet Testing Program

50,000 Miles Conversion Efficiency Test
Pollutant Carbon Monoxide

Model	Conversion Efficiency 50,000 miles EEE	HT3	Sign	------ Rank Sum Test ------ Test Statistic	Mean	Sig.Level (%)(b)	T-test Sig.Level (%)(b)
D	0.606	0.593	-	5.0	3.0	90.00	85.37
E	0.489	0.538	+	0.0	4.5	5.00	1.34
T	0.610	0.647	+	2.0	4.5	20.00	22.97
C	0.706	0.654	-	7.0	4.5	90.00	84.66
G	0.690	0.738	+	4.0	4.5	50.00	22.53
H	0.712	0.742	+	2.0	4.5	20.00	12.35
I	0.786	0.790	+	4.0	4.5	50.00	35.38
Weighted Average(c)	0.678	0.696	+				6.87
Total				24.0	30.0	15.35	

EPA Sign Test: Observation of 5 '+' sign(s) in 7 trials rejects the hypothesis of no beneficial HiTEC 3000 effect at the 22.66 percent significance level(b).

EPA Overall Rank Sum Test: The hypothesis of no beneficial HiTEC 3000 effect is reject at the 15.35 percent significance level(b).

Weighted Average Test: The hypothesis of no beneficial HiTEC 3000 effect is rejected at the 6.87 percent significance level(b).

Notes:
a. Each figure is the mean of the conversion efficiencies at 50,000 miles for each fuel.
b. The lower the significance level, the greater the evidence of a beneficial HiTEC 3000 effect.
c. The weights for the weighted averages are proportional to 1988 sales figures.

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Ethyl Corporation HiTEC 3000 Fleet Testing Program

50,000 Miles Conversion Efficiency Test
Pollutant Nitrogen Oxides

Model	Conversion Efficiency 50,000 miles EEE	HT3	Sign	------ Rank Sum Test ------ Test Statistic	Mean	Sig.Level (%)(b)	T-test Sig.Level (%)(b)
D	0.778	0.714	-	6.0	3.0	100.00	99.52
E	0.780	0.789	+	3.0	4.5	35.00	33.29
T	0.795	0.827	+	2.0	4.5	20.00	8.95
C	0.832	0.891	+	0.0	4.5	5.00	6.61
G	0.734	0.729	-	5.0	4.5	65.00	56.76
H	0.606	0.684	+	2.0	4.5	20.00	12.10
I	0.759	0.778	+	4.0	4.5	50.00	21.29
Weighted Average(c)	0.731	0.767	+				2.13
Total				22.0	30.0	8.66	

EPA Sign Test: Observation of 5 '+' sign(s) in 7 trials rejects the hypothesis of no beneficial HiTEC 3000 effect at the 22.66 percent significance level(b).

EPA Overall Rank Sum Test: The hypothesis of no beneficial HiTEC 3000 effect is reject at the 8.66 percent significance level(b).

Weighted Average Test: The hypothesis of no beneficial HiTEC 3000 effect is rejected at the 2.13 percent significance level(b).

Notes:
a. Each figure is the mean of the conversion efficiencies at 50,000 miles for each fuel.
b. The lower the significance level, the greater the evidence of a beneficial HiTEC 3000 effect.
c. The weights for the weighted averages are proportional to 1988 sales figures.

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Ethyl Corporation HiTEC 3000 Fleet Testing Program

75,000 Miles Conversion Efficiency Test
Pollutant Hydrocarbons

Model	Conversion Efficiency 75,000 miles EEE	HT3	Sign	Rank Sum Test Test Statistic	Mean	Sig.Level (%)(b)	T-test Sig.Level (%)(b)
D	0.729	0.742	+	3.0	3.0	60.00	38.69
E	0.855	0.867	+	5.0	4.5	65.00	31.20
T	0.823	0.857	+	0.0	4.5	5.00	0.07
C	0.868	0.864	-	6.0	4.5	80.00	60.80
G	0.860	0.864	+	5.0	4.5	65.00	37.82
H	0.852	0.856	+	4.0	4.5	50.00	37.09
Weighted Average(c)	0.844	0.854	+				5.73
Total				23.0	25.5	32.20	

EPA Sign Test: Observation of 5 '+' sign(s) in 6 trials rejects the hypothesis of nc beneficial HiTEC 3000 effect at the 10.94 percent significance level(b).

EPA Overall Rank Sum Test: The hypothesis of no beneficial HiTEC 3000 effect is reject at the 32.20 percent significance level(b).

Weighted Average Test: The hypothesis of no beneficial HiTEC 3000 effect is rejected at the 5.73 percent significance level(b).

Notes:
a. Each figure is the mean of the conversion efficiencies at 75,000 miles for each fuel.
b. The lower the significance level, the greater the evidence of a beneficial HiTEC 3000 effect.
c. The weights for the weighted averages are proportional to 1988 sales figures.

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Ethyl Corporation HiTEC 3000 Fleet Testing Program

75,000 Miles Conversion Efficiency Test
Pollutant Carbon Monoxide

Model	Conversion Efficiency 75,000 miles			------ Rank Sum Test ------			T-test
	EEE	HT3	Sign	Test Statistic	Mean	Sig.Level (%)(b)	Sig.Level (%)(b)
D	0.567	0.575	+	2.0	3.0	40.00	35.22
E	0.467	0.478	+	5.0	4.5	65.00	41.45
T	0.583	0.668	+	0.0	4.5	5.00	0.27
C	0.557	0.537	-	5.0	4.5	65.00	60.24
G	0.658	0.599	-	8.0	4.5	95.00	92.23
H	0.672	0.685	+	3.0	4.5	35.00	33.44
Weighted Average(c)	0.600	0.613	+				23.95
Total				23.0	25.5	32.20	

EPA Sign Test: Observation of 4 '+' sign(s) in 6 trials rejects the hypothesis of nc beneficial HiTEC 3000 effect at the 34.38 percent significance level(b).

EPA Overall Rank Sum Test: The hypothesis of no beneficial HiTEC 3000 effect is reject at the 32.20 percent significance level(b).

Weighted Average Test: The hypothesis of no beneficial HiTEC 3000 effect is rejected at the 23.95 percent significance level(b).

Notes:

a. Each figure is the mean of the conversion efficiencies at 75,000 miles for each fuel.

b. The lower the significance level, the greater the evidence of a beneficial HiTEC 3000 effect.

c. The weights for the weighted averages are proportional to 1988 sales figures.

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Ethyl Corporation HiTEC 3000 Fleet Testing Program

75,000 Miles Conversion Efficiency Test
Pollutant Nitrogen Oxides

Model	Conversion Efficiency 75,000 miles EEE	HT3	Sign	------ Rank Sum Test ------ Test Statistic	Mean	Sig.Level (%)(b)	T-test Sig.Level (%)(b)
D	0.769	0.740	-	5.0	3.0	90.00	82.93
E	0.780	0.806	+	4.0	4.5	50.00	25.87
T	0.794	0.841	+	0.0	4.5	5.00	0.54
C	0.756	0.839	+	0.0	4.5	5.00	2.22
G	0.695	0.637	-	7.0	4.5	90.00	90.38
H	0.625	0.766	+	0.0	4.5	5.00	0.01
Weighted Average(c)	0.714	0.780	+				0.00
Total				16.0	25.5	3.95	

EPA Sign Test: Observation of 4 '+' sign(s) in 6 trials rejects the hypothesis of nc beneficial HiTEC 3000 effect at the 34.38 percent significance level(b).

EPA Overall Rank Sum Test: The hypothesis of no beneficial HiTEC 3000 effect is reject at the 3.95 percent significance level(b).

Weighted Average Test: The hypothesis of no beneficial HiTEC 3000 effect is rejected at the 0.00 percent significance level(b).

Notes:
a. Each figure is the mean of the conversion efficiencies at 75,000 miles for each fuel.
b. The lower the significance level, the greater the evidence of a beneficial HiTEC 3000 effect.
c. The weights for the weighted averages are proportional to 1988 sales figures.

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4

Analysis of the Ford Submitted Data

As a part of their comments Ford Motor Company submitted detailed compositional analysis and microreactor conversion efficiency data for two series of catalysts removed from Canadian automobiles. The first series of 11 catalysts were removed from 10 Ford of Canada employees cars that had no reported/detectable mechanical or operational problems. The second series of 26 catalysts were from 13 Canadian automobiles with operational problems repaired by Ford dealers.

The microreactor used for determining the catalyst activity employs a small "button" (1/2" diameter x 1/2" high cylinder) removed from the approximate center of the monolith. The sampling technique removes a 1/2" diameter "button" from the monolith inlet, middle and outlet. The inlet "button" is then used in the microreactor procedure to determine conversion efficiency for the three regulated pollutants hydrocarbons, carbon monoxide and nitrogen oxide. Each of the three buttons is analyzed by the B.E.T. adsorption technique to determine the surface area and by XRF technique to determine the metals content. The inlet, middle and outlet sample results show "profiles" of surface area and composition in the gas flow direction. The profiles for contamination (Pb, Zn, Ba, etc.) concentrations generally show much higher levels on the inlet sample than either the middle or outlet sample. If, as generally accepted, these contaminants adversely affect catalyst activity, a regression analysis should separate the individual relationships without the "noise" of other effect to confuse the issue. It cannot be emphasized too often nor too strongly that the collection of catalysts are <u>not representative</u> of the population of automobiles in service since 13 of 23 automobiles were known to have catalyst related deficiencies. The 10 automobiles from Ford employees may or may not have been in need of repair. This question was examined by a separate analysis of these automobiles. The number of observations is reduced and it is difficult to see any additional information from this analysis.

The microreactor procedure determined conversion efficiencies at a gas inlet temperature of approximately 550°C for redox ratios from about 0.8 to 1.85. The reason for evaluating such fuel rich regions (R much greater than 1) is not clear. The primary region of interest is about R = 1. Data analyses were conducted for redox ration of 1.0. There were some differences in the significance levels of variables but overall: 1) the expected poisons (Ba, Zn and Pb) showed varying degrees of catalyst poisoning; 2) when the levels of catalyst metals varied significantly the effects were noticeable on catalyst efficiency [1] (Ce, Ni are particularly of note); 3) Manganese does not reduce the

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[1] This is important because it indicates that the analysis is sensitive enough to find intentional changes to catalyst formulations made by manufacturer.

conversion efficiency for hydrocarbon, carbon monoxide or nitrogen oxide, and in fact shows moderate improvement for hydrocarbon and carbon monoxide.

The data analysis results for redox ratio = 1.0 gave variables and significance levels as shown in Table 1. The hydrocarbon results show Lead and Zinc to be highly significant poisons (denoted by the negative sign of the coefficient) and surface area and manganese to be significant positive correlates. Carbon monoxide results reveal that Barium, Iron, Miles, and Zinc significantly reduce conversion efficiency and Surface Area, Nickel, Cerium, and Manganese increase conversion efficiency. Barium and Lead significantly reduce, while Surface Area, Nickel and Sulfur significantly increase nitrogen oxide conversion efficiency. The regression models explained large fractions of the error varying from about 0.80 for the nitrogen oxide regression to about 0.90 for the hydrocarbon regression. The Nickel and Cerium are believed to be part of the catalyst wash coat formulations (as opposed to Lead e.g. which is a contaminant). These components appeared in the catalysts at two distinct levels and it is not clear if this represents some predictable catalyst phenomenon or is indicative of changed catalyst formulation. In either event the regression technique was capable of detecting the significance of the changes. The positive effect of Sulfur in nitrogen oxide conversion efficiency is surprising but may be an artifact because of the many zero levels of sulfur reported. Figure 1 shows the percent increase in HC (hydrocarbon) conversion efficiency for each significant regression variable as listed on the y-axis. The units of measure for each regression variable and its minimum and maximum values are also shown along the y-axis. The average is shown on the x-axis as the mid tick mark flanked on each side by the 95% confidence limits. To illustrate how to use these somewhat complex but highly informative charts consider the data for manganese. The y-axis data shows that the units of measure for the Mn variable is wt.%; the minimum wt.% in the data is 0.05 and the maximum wt.% is 6.3. The average percent increase in HC conversion efficiency is about 28 with lower and upper 95% confidence limits of about 0 and 55, respectively. X-axis values greater than zero indicate improved catalyst conversion efficiency and values less than zero indicate degraded catalyst conversion efficiency. A cursory glance shows that Manganese and Surface Area improve conversion efficiency and Lead and Zinc degrade conversion efficiency.

Figure 2 shows main effects for carbon monoxide. Manganese, Cerium, Nickel and Surface Area improve conversion efficiency while Barium, Iron, Zinc, and Miles on Car degrade conversion efficiency.

Figure 3 shown main effects for nitrogen oxide. Sulfur, Nickel and Surface Area improve conversion efficiency and Barium and Lead degrade conversion efficiency.

TABLE 1

Regression Summaries for Redox Ratio = 1

Independent Variable	Variable ID	Coeff. Value	Standard Error	Significance Level
Hydrocarbon*				
	Intercept	70.66	8.80	-
	Surface Area**	1.02	0.40	0.021
	Lead	-17.04	4.23	0.001
	Zinc	-91.75	21.60	0.001
	Manganese	4.46	2.08	0.046
R-sq. = 0.806; RMS Error = 6.794				
Carbon Monoxide*				
	Intercept	87.83	5.55	-
	Surface Area**	0.48	0.19	0.022
	Nickel	14.50	3.39	0.001
	Cerium	2.85	0.77	0.002
	Barium	-14.51	6.87	0.053
	Iron	-20.88	9.47	0.045
	Zinc	-19.31	8.76	0.045
	Manganese	3.57	0.93	0.002
	Miles	-0.000283	0.000071	0.001
R-sq. = 0.739; RMS Error = 2.144				
Nitrogen Oxide*				
	Intercept	90.06	31.95	-
	Surface Area**	2.26	0.94	0.028
	Nickel	49.46	14.07	0.003
	Barium	-127.23	56.55	0.001
	Lead	144.55	11.69	0.001
	Sulfur	232.12	103.77	0.039
R-sq. = 0.647; RMS Error = 18.23				

* - The independent variables are in conversion efficiency for the stated pollutant.

**- B.E.T. values in sq. m per gram.

Figures 4,5,6, and 7 show hydrocarbon conversion efficiencies for each of the significant regression variables. Every plot is adjusted with the regression model for each of the remaining variables. This results in a depiction of the relationship independent of the scatter introduced by other variables. Zinc, shown in Figure 4, shows that the data is evenly distributed over the range of dependent variables (i.e. not concentrated in clusters). The Lead plot (Figure 5) is different from Zinc in that most of the data is clustered at values less than about 0.25 with only three points at 1.2 and greater which would suggest a higher influence on slope for these points. Surface Area and Manganese plots (Figures 6 and 7) show acceptable distributation like the Zinc curve. The general conclusion is that except for Lead, the dataset was well-conditioned to detect the relationships between the regression variables.

Figures 8 through 15 show adjusted plots for Carbon Monoxide for each one of the significant regression variables. The "clustering" of the data for Nickel and Cerium are seen graphically in Figures 8 and 11, respectively. This is assumed to indicate changes in catalyst formulation rather than in service effect.

Figures 16 through 20 show adjusted plots for nitrogen oxide for each one of the significant regression variables. The plot with lead (Figure 16) exhibits once again the large leverage of the three data points at lead values greater than 1.2. The clustering of the data for Nickel are evident in Figure 17. The effect of Sulfur is somewhat surprising but is greatly influenced by the large number of zero values reported for Sulfur. Expectation would be that the effect would vanish if sufficient numbers of samples were included.

Conclusions:

The microreactor measures of activity when combined with the composition data for the inlet samples provide the tools for determining what components actually degrade or improve catalyst conversion efficiency. The regression analysis provides the means for separating the effects for separate components. It is remarkable that in such random collections of catalysts the results can be correlated as well as is shown. The accepted poisons (PB, Zn and sometimes FE) indeed show up as degrading catalyst conversion efficiency and the known promoters (Ni, CE and Surface Area) are shown as improving conversion efficiency. Manganese is not shown to degrade catalyst conversion efficiency. Similar results are seen when the integrated conversion efficiency is used as the independent variable. These results were not reported herein but are available if they are desired.

FIGURE 1

Mulreg FORT1233, Model FORT12332
Main Effects on Response HC
(with 95% Confidence Intervals)

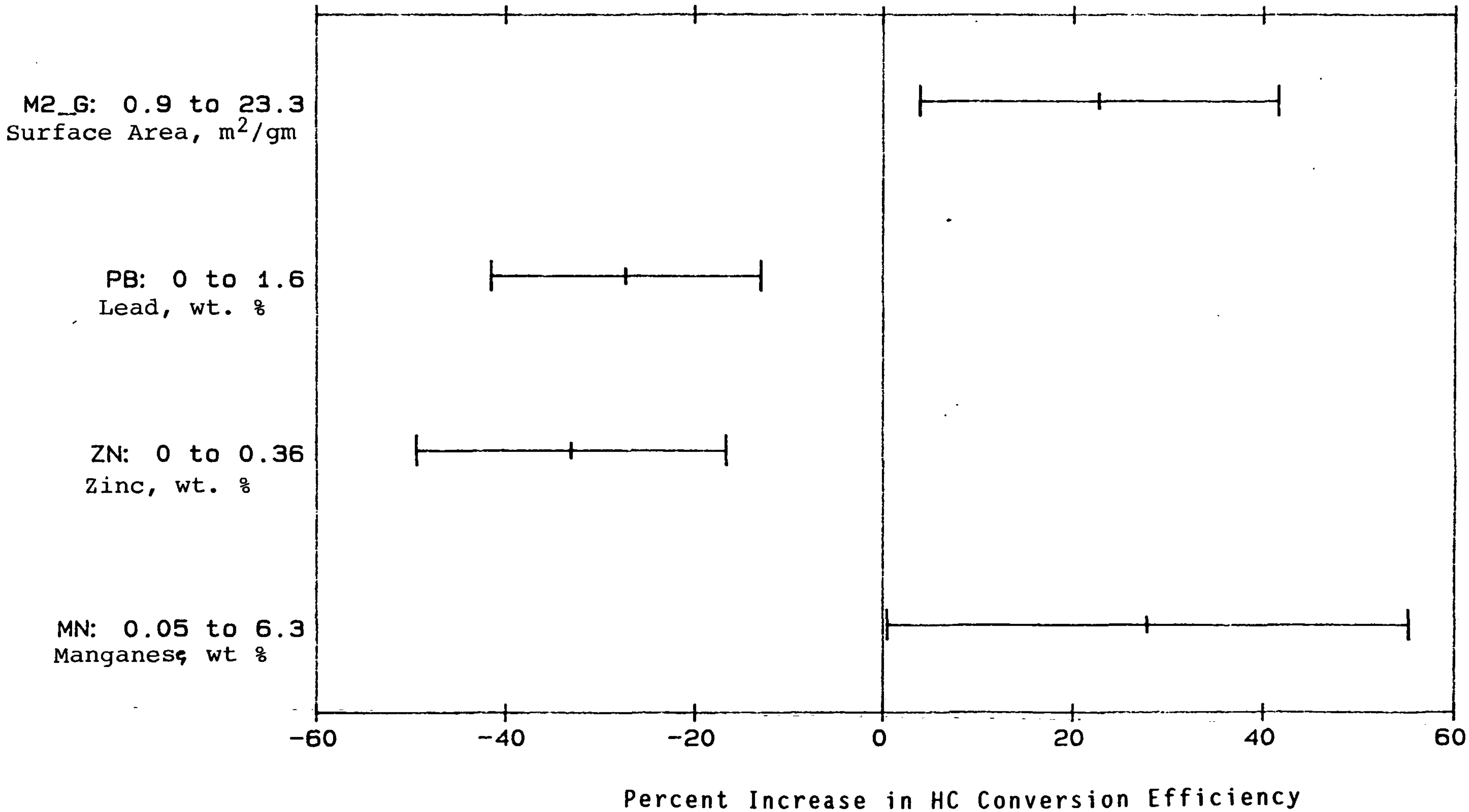


FIGURE 2

Mulreg FORT1233, Model FORT12333
Main Effects on Response CO
(with 95% Confidence Intervals)

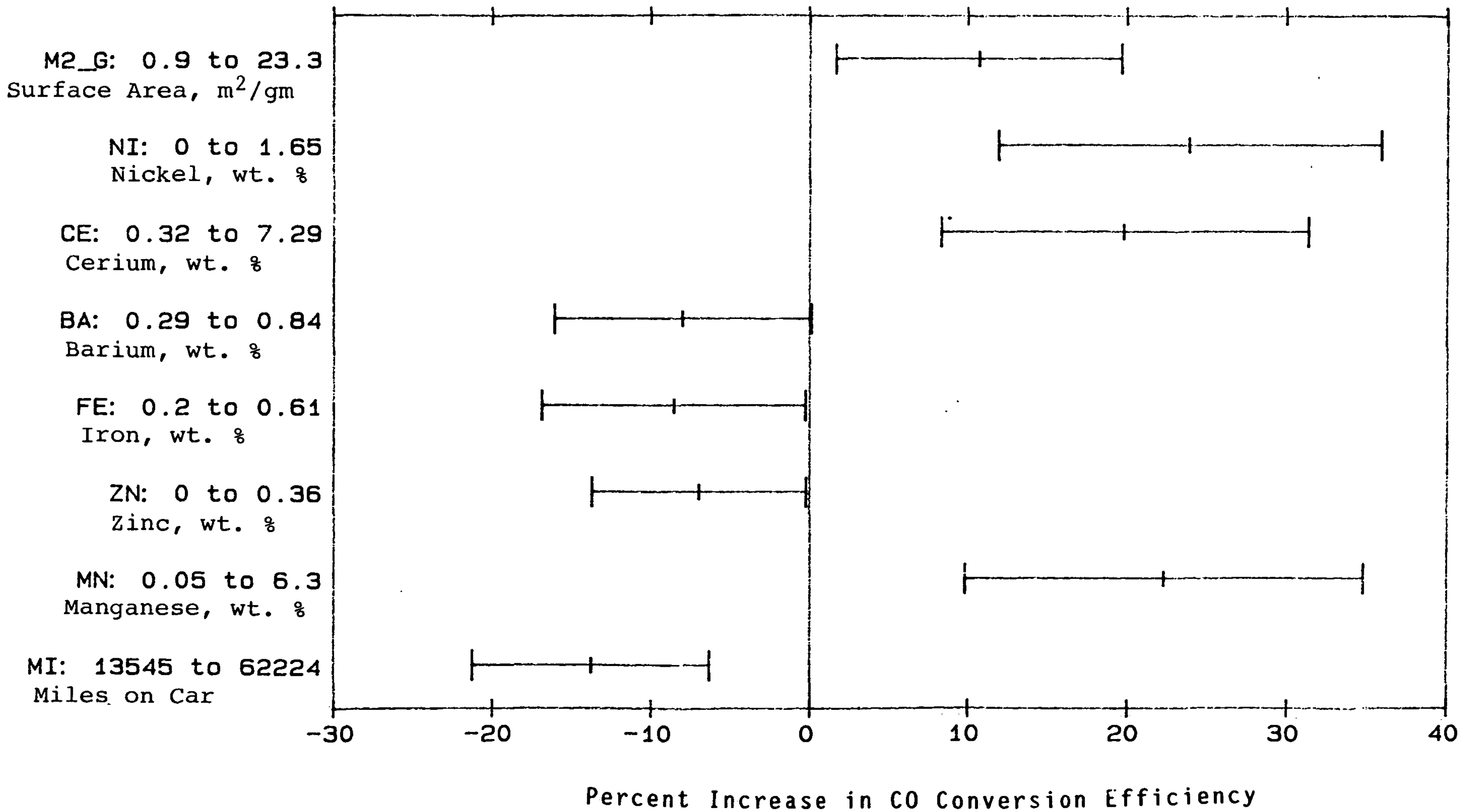
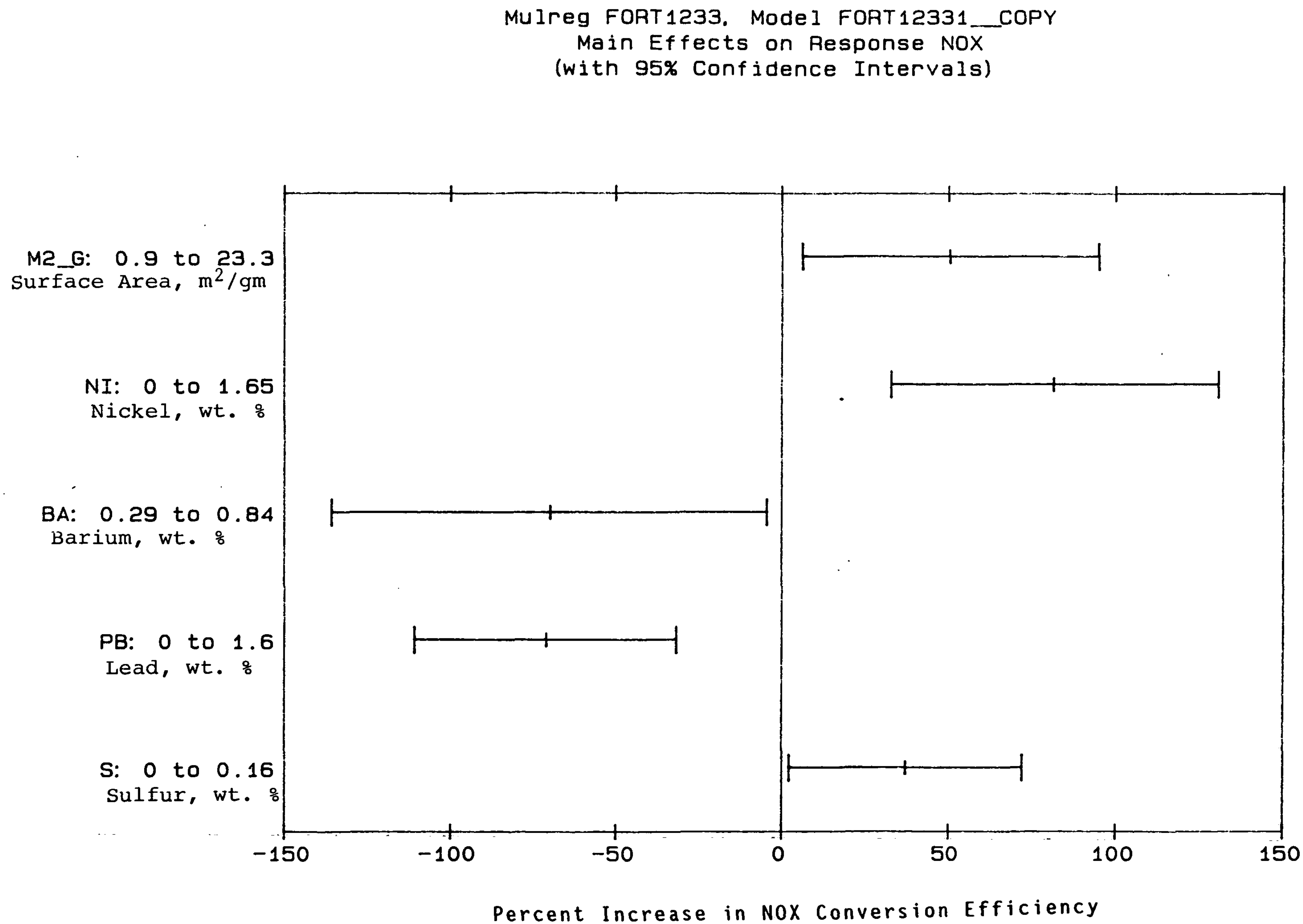


FIGURE 3



Mulreg FORT1233, Model FORT12331__COPY
Main Effects on Response NOX
(with 95% Confidence Intervals)
M2_G: 0.9 to 23.3
Surface Area, m2/gm
NI: 0 to 1.65
Nickel, wt. %
BA: 0.29 to 0.84
Barium, wt. %
PB: 0 to 1.6
Lead, wt. %
S: 0 to 0.16
Sulfur, wt. %
-150
-100
-50
0
50
100
150
Percent Increase in NOX Conversion Efficiency

FIGURE 4

Graph: 49369 06-AUG-90 15: 15 Page 1

HC vs ZN, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12332

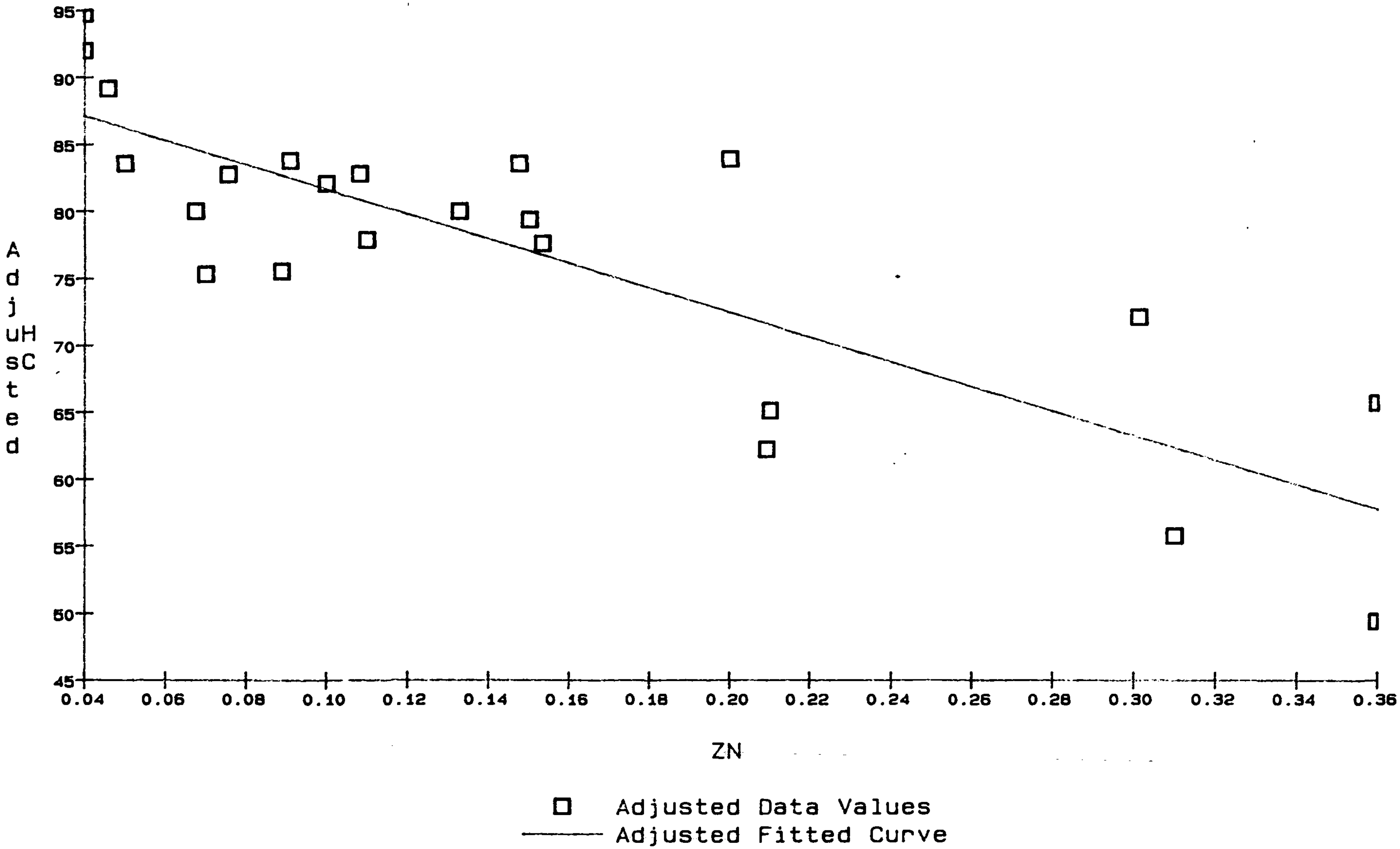


FIGURE 5

Graph: 49378

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HC vs PB, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12332

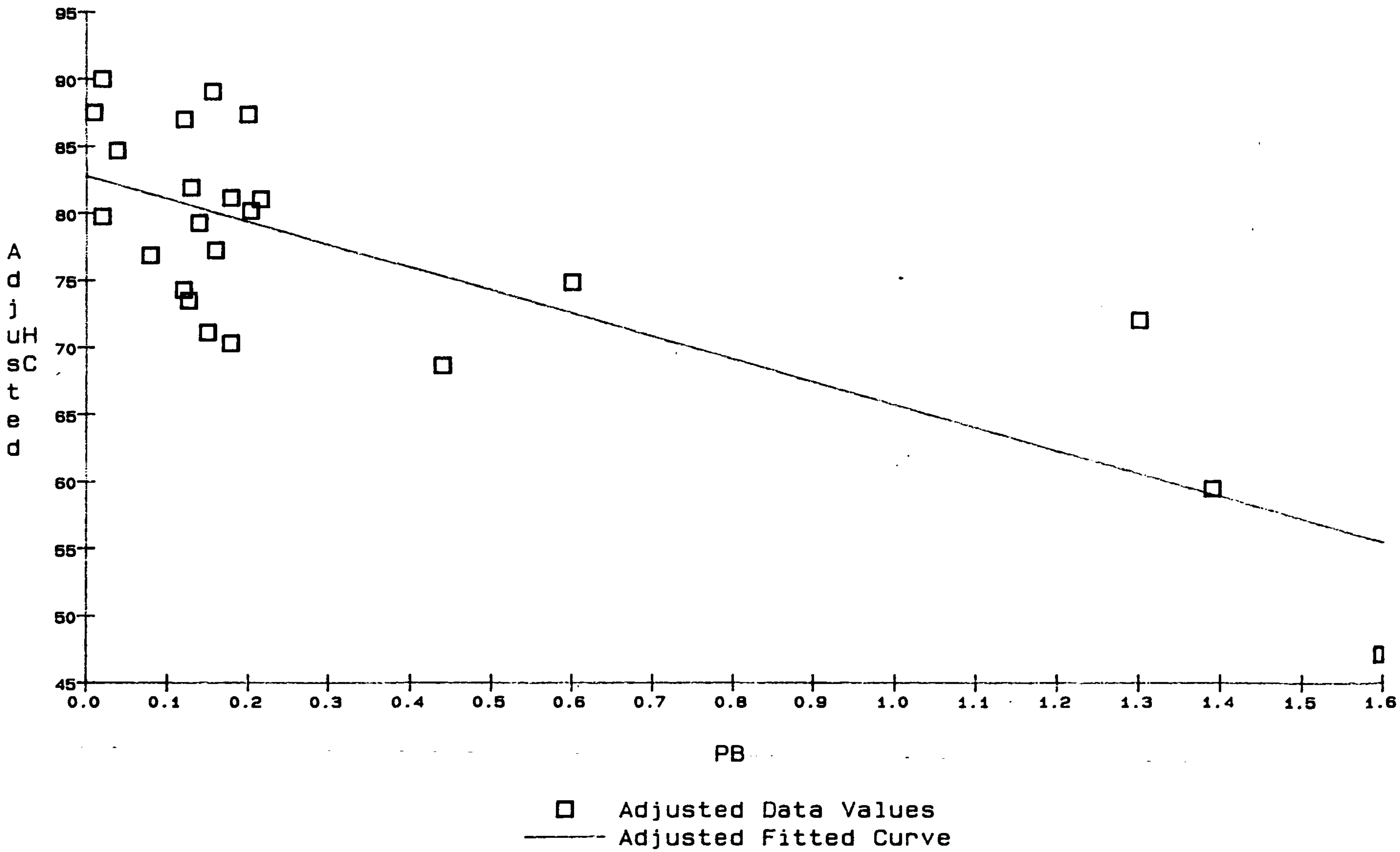

FIGURE 6

Graph: 49387

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HC vs M2_G, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12332

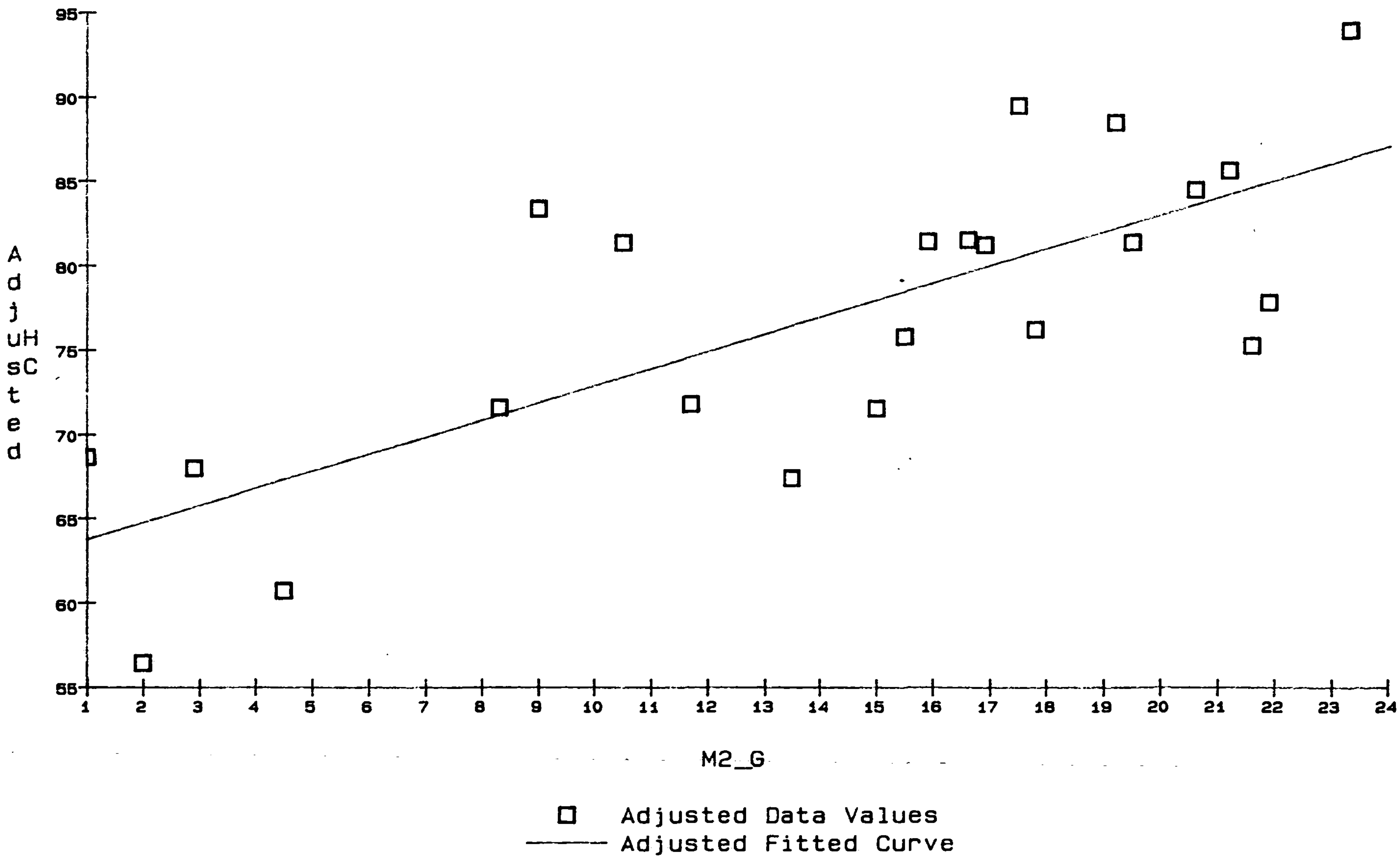

FIGURE 7

Graph: 49360

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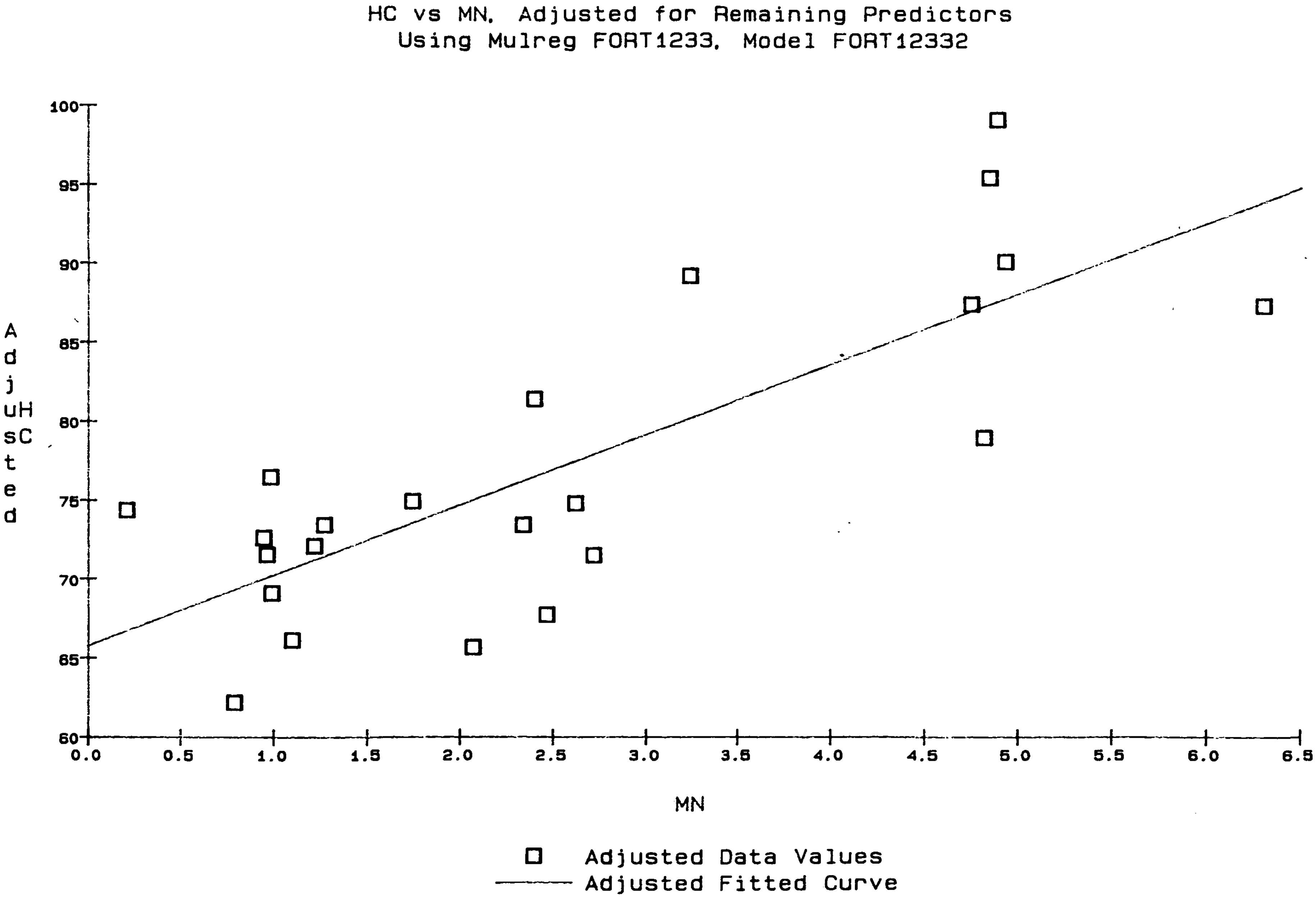

FIGURE 8

Graph: 49388

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CO vs NI, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12333

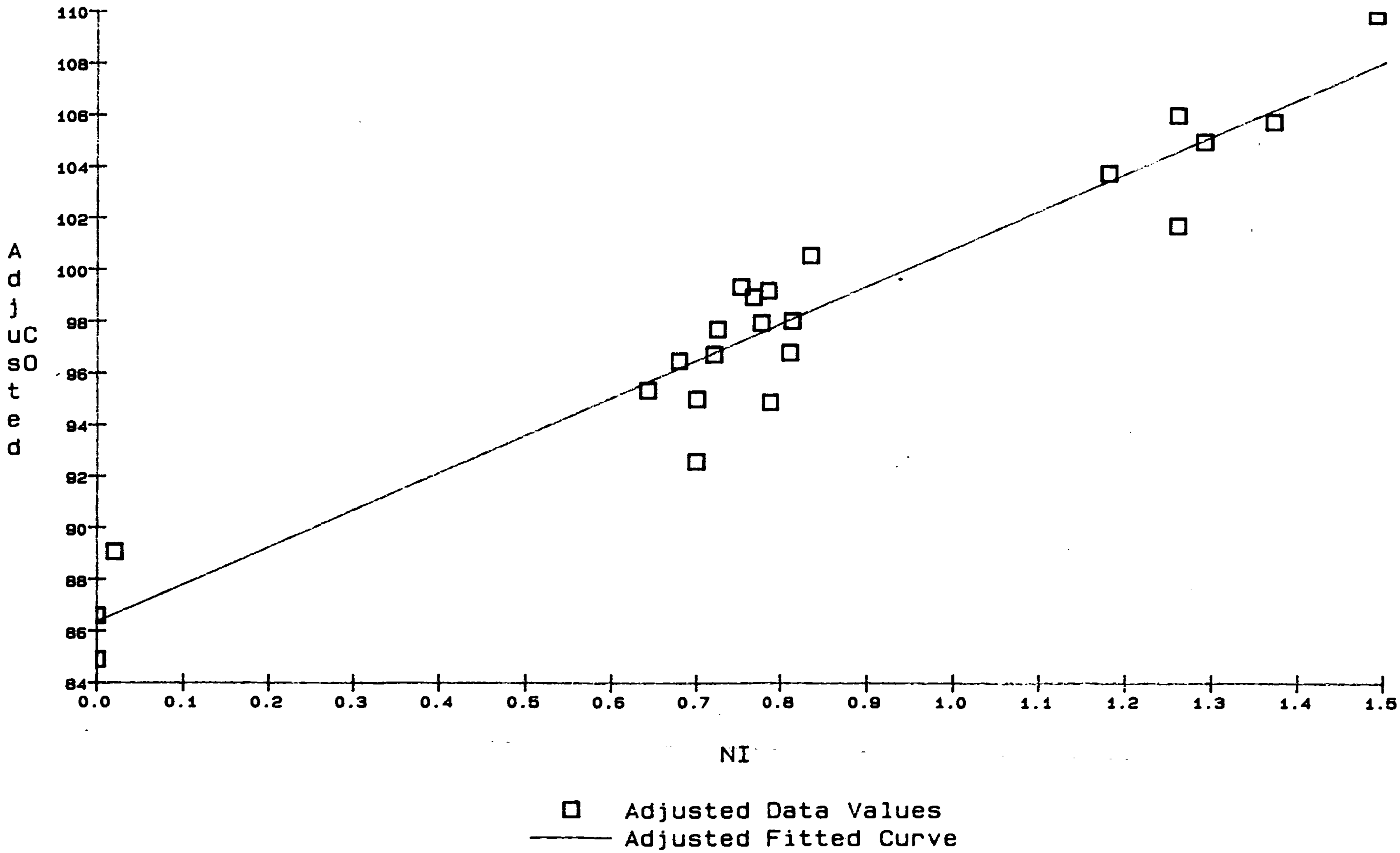

FIGURE 9

Graph: 49370

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CO vs MILES, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12333

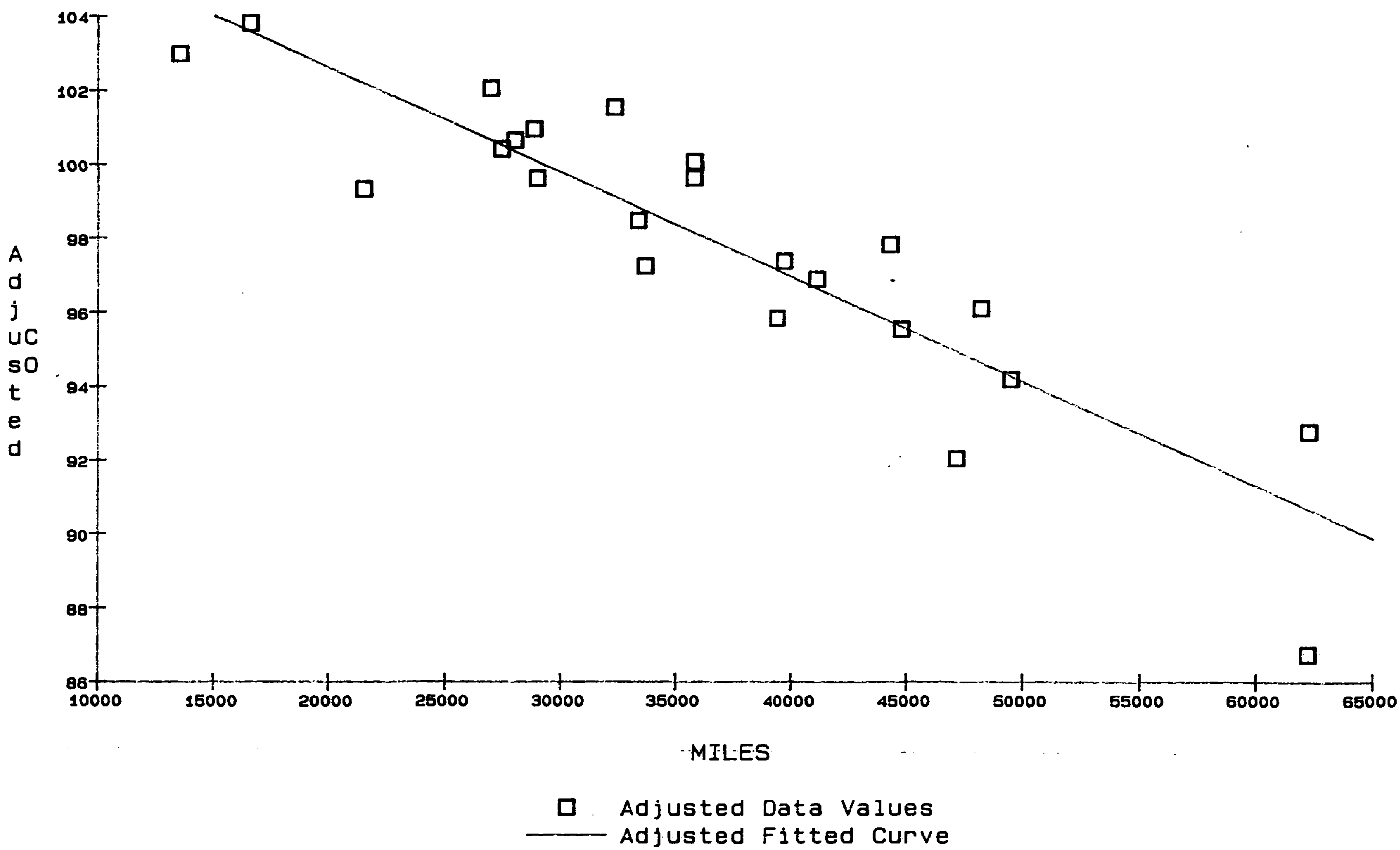

FIGURE 10

Graph: 49361

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CO vs MN, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12333

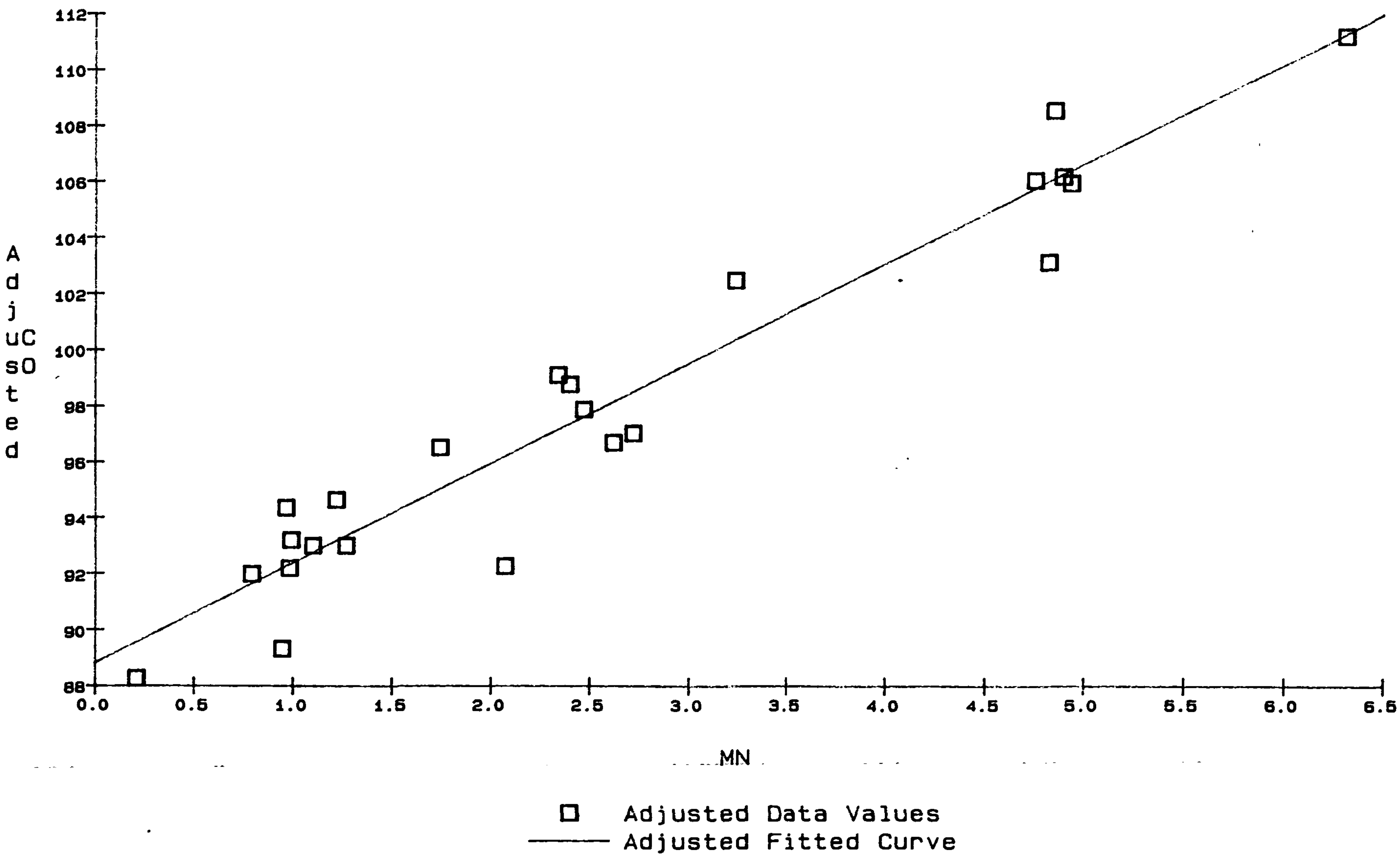


FIGURE 11

Graph: 49397

06-AUG-90 15: 37 Page 1

CO vs CE, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12333

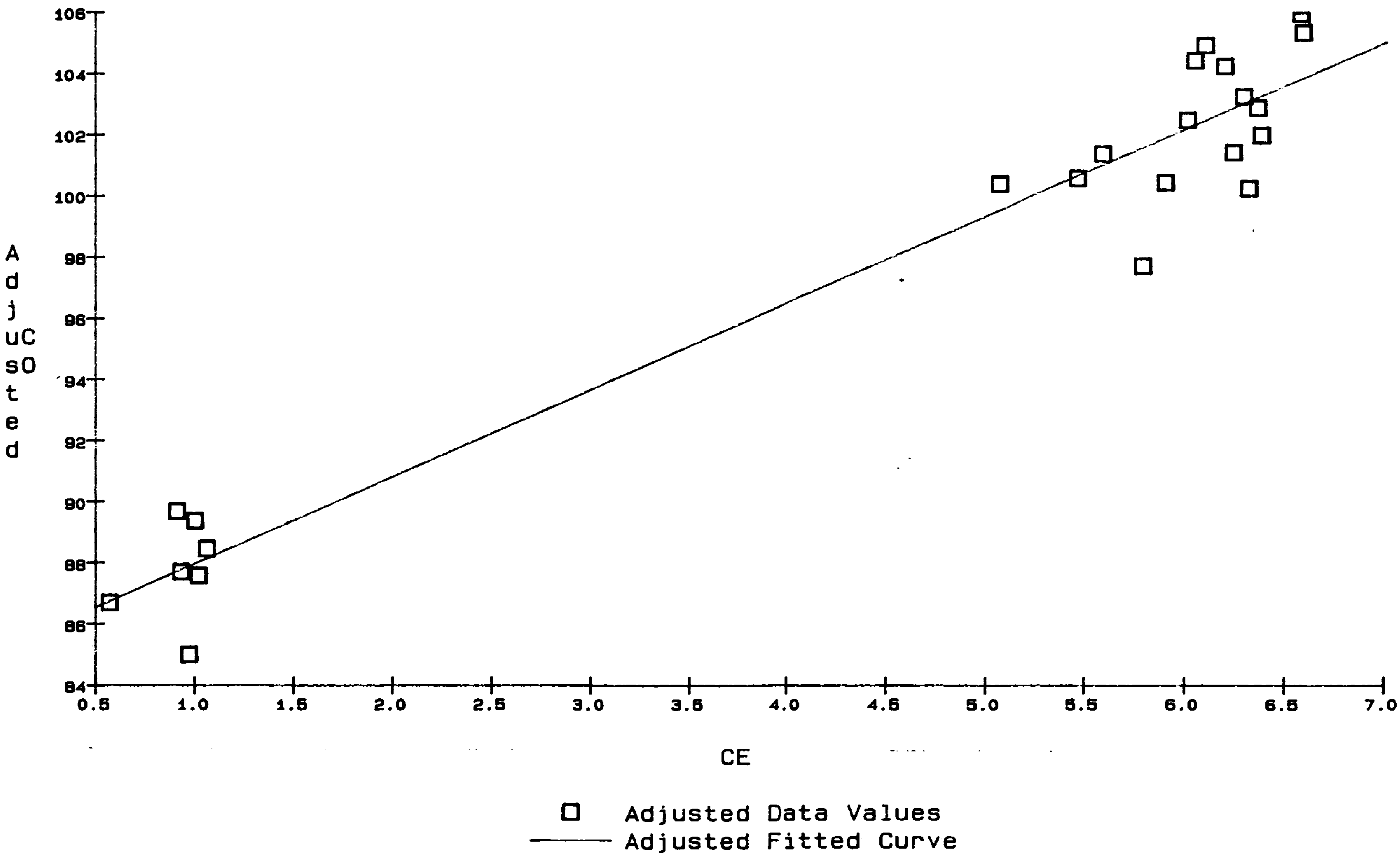


FIGURE 12

Graph: 49297

08-AUG-90 13:05 Page 1

CO vs M2_G, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12333

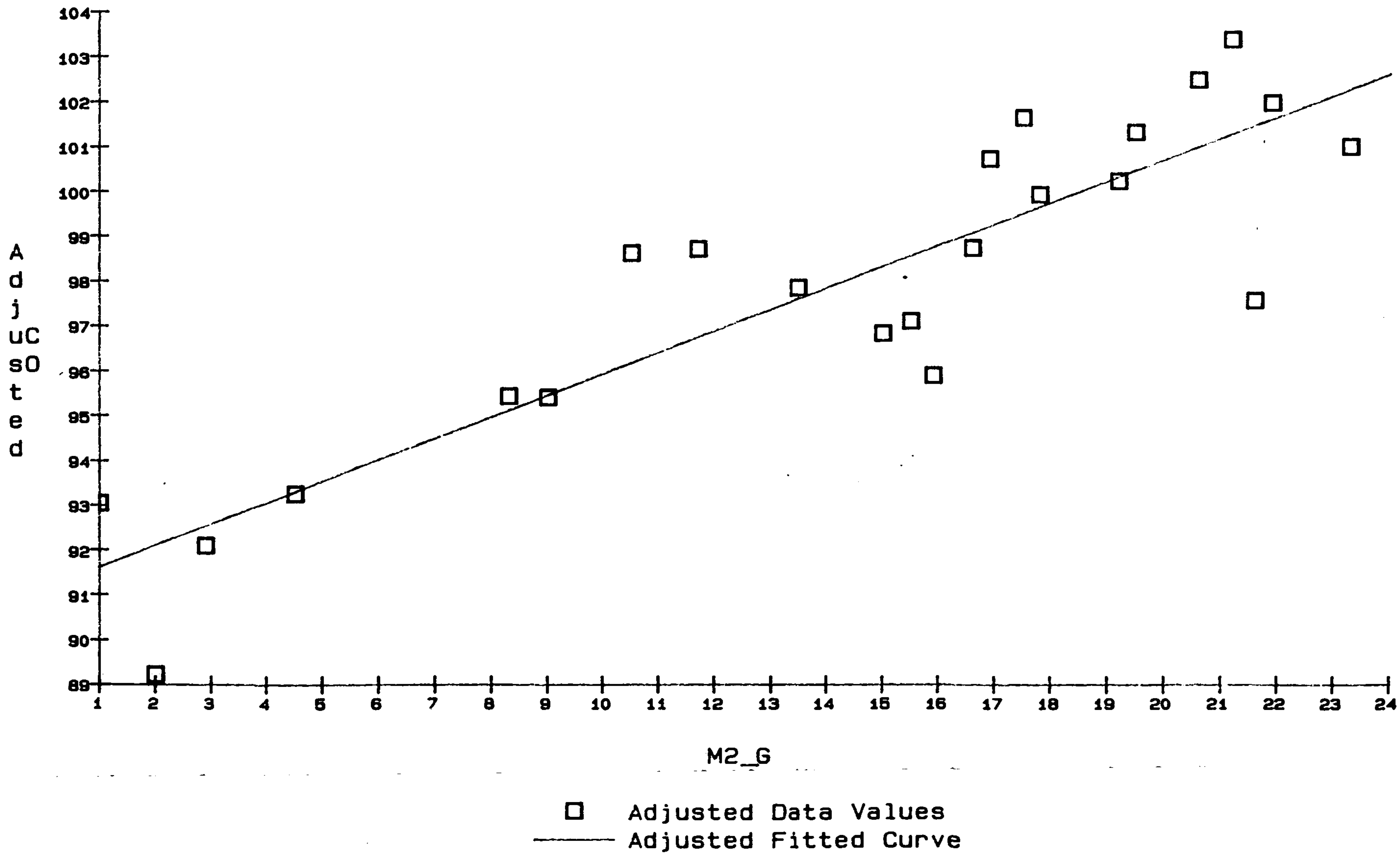


FIGURE 13

Graph: 49333

08-AUG-90 13:11 Page 1

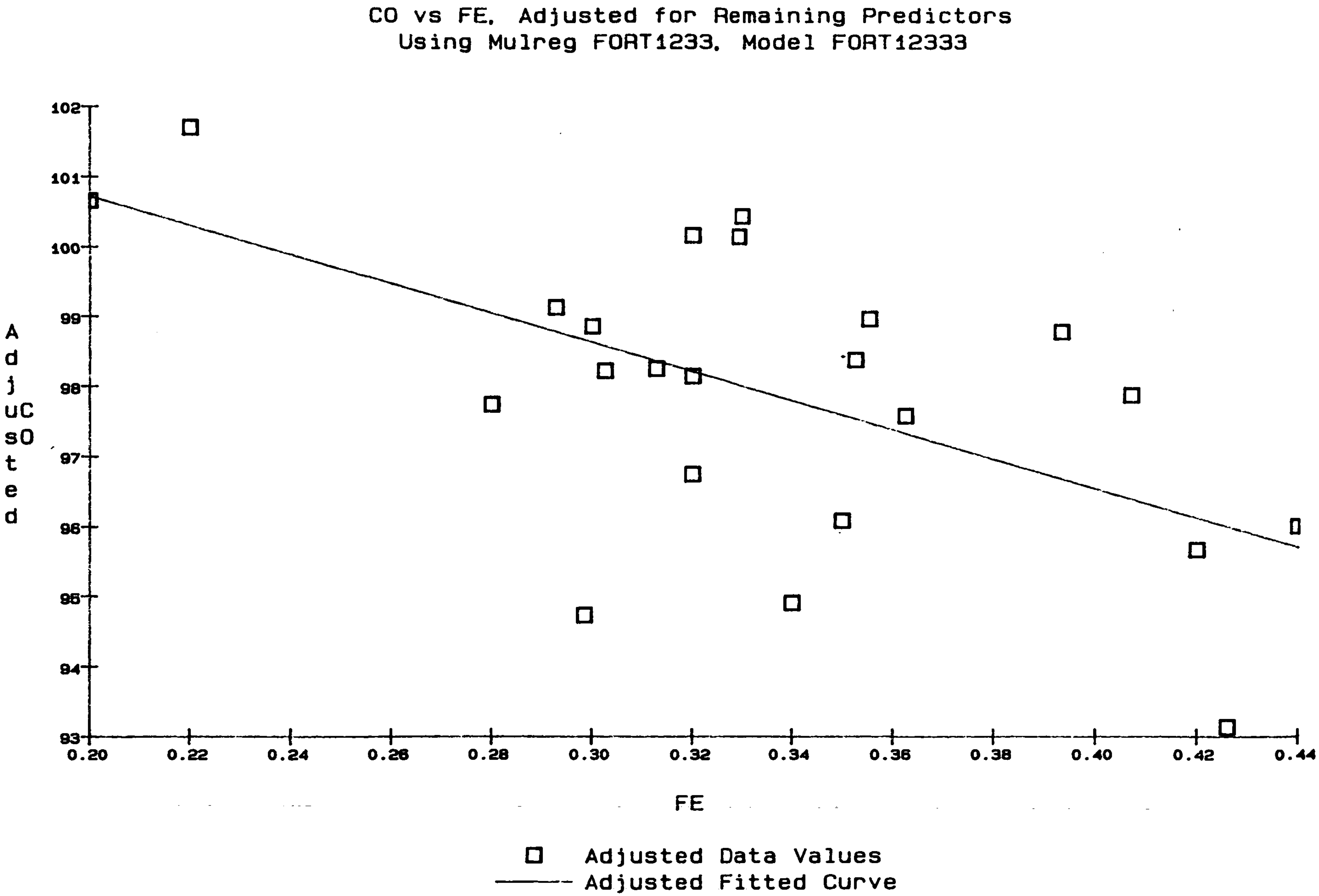


FIGURE 14

Graph: 49342 08-AUG-90 13:13 Page 1

CO vs ZN, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12333

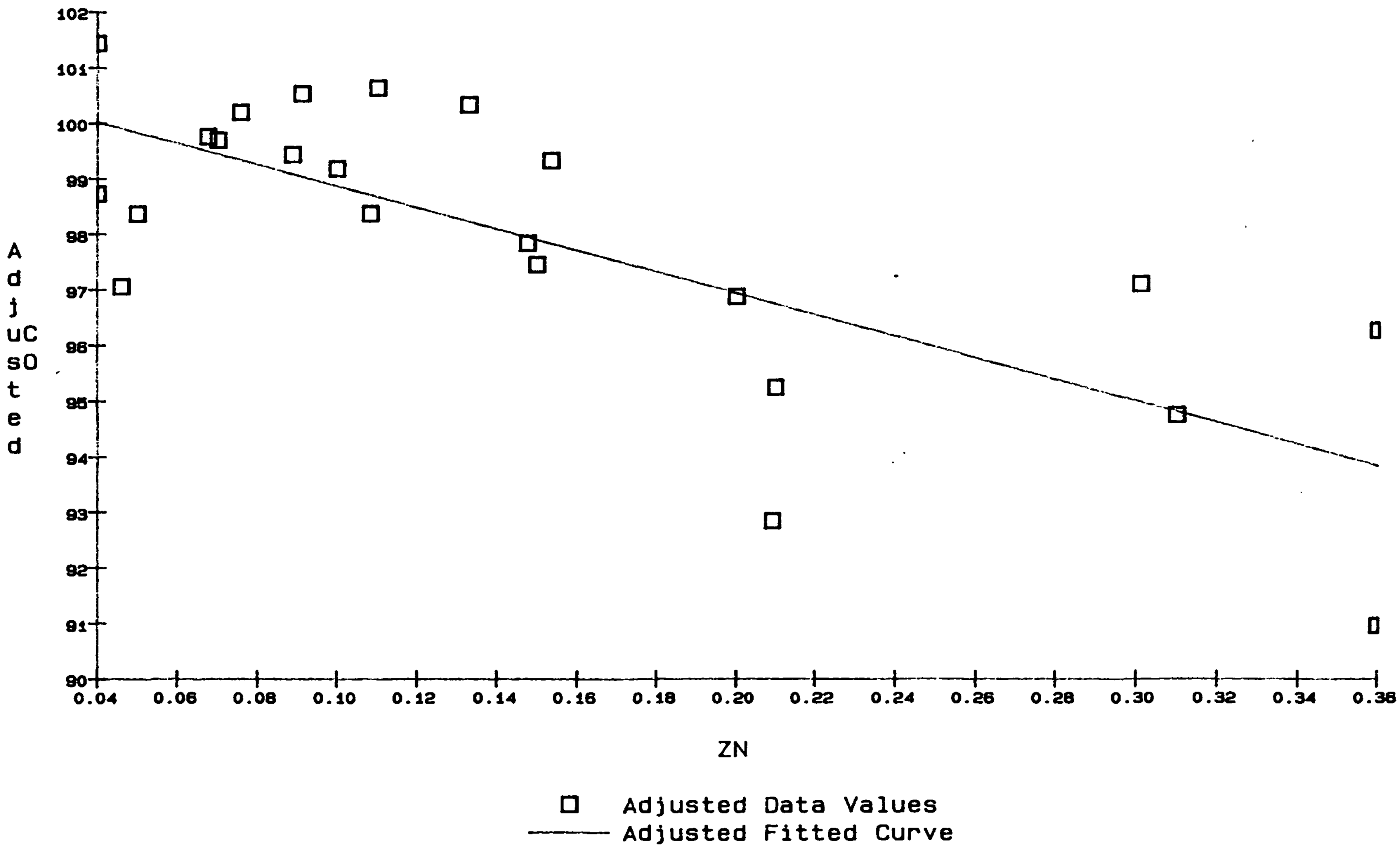


FIGURE 15

Graph: 49324

08-AUG-90 13:09 Page 1

CO vs BA, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12333

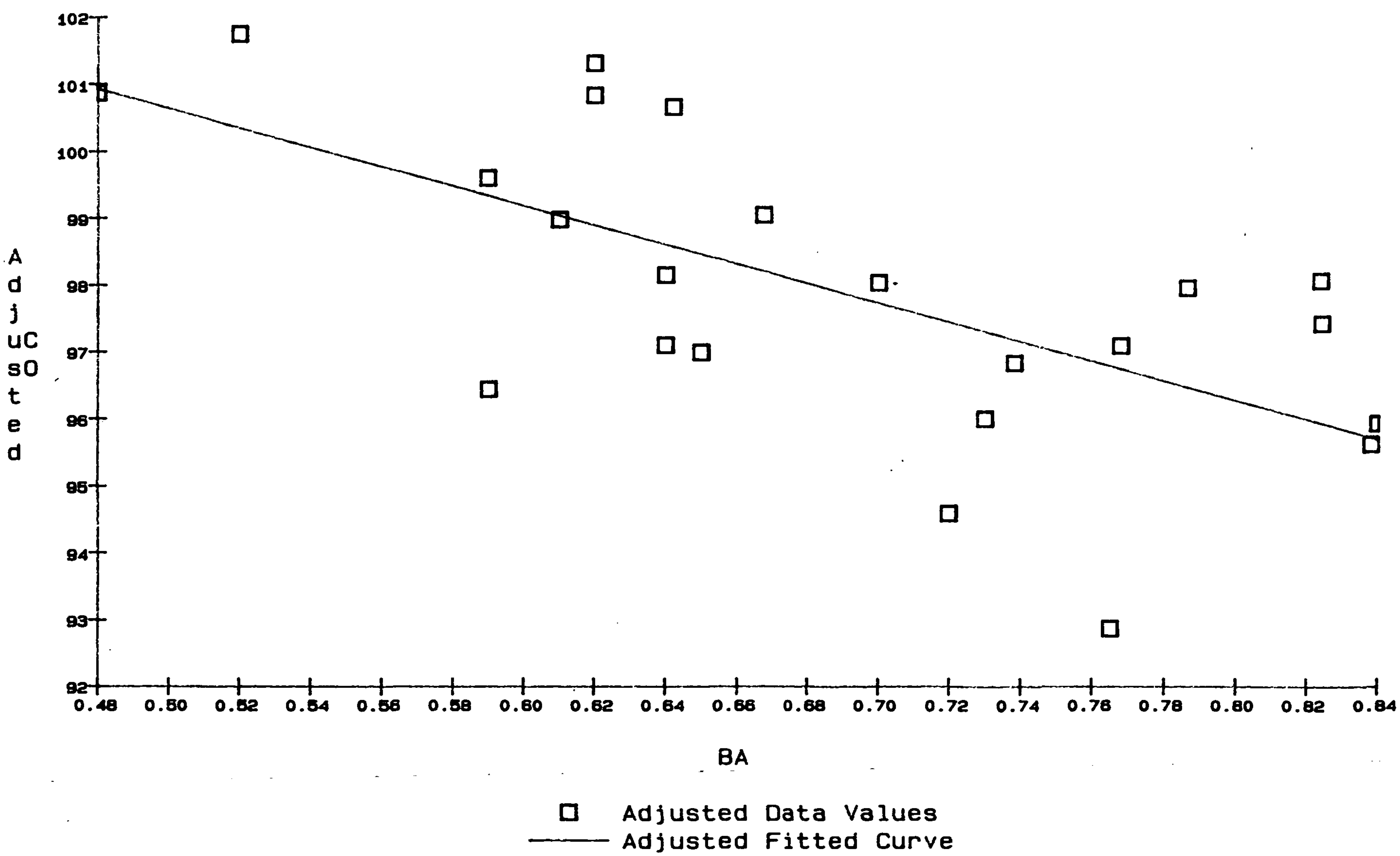


FIGURE 16

Graph: 49325

08-AUG-90 13:30 Page 1

NOX vs PB, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12334

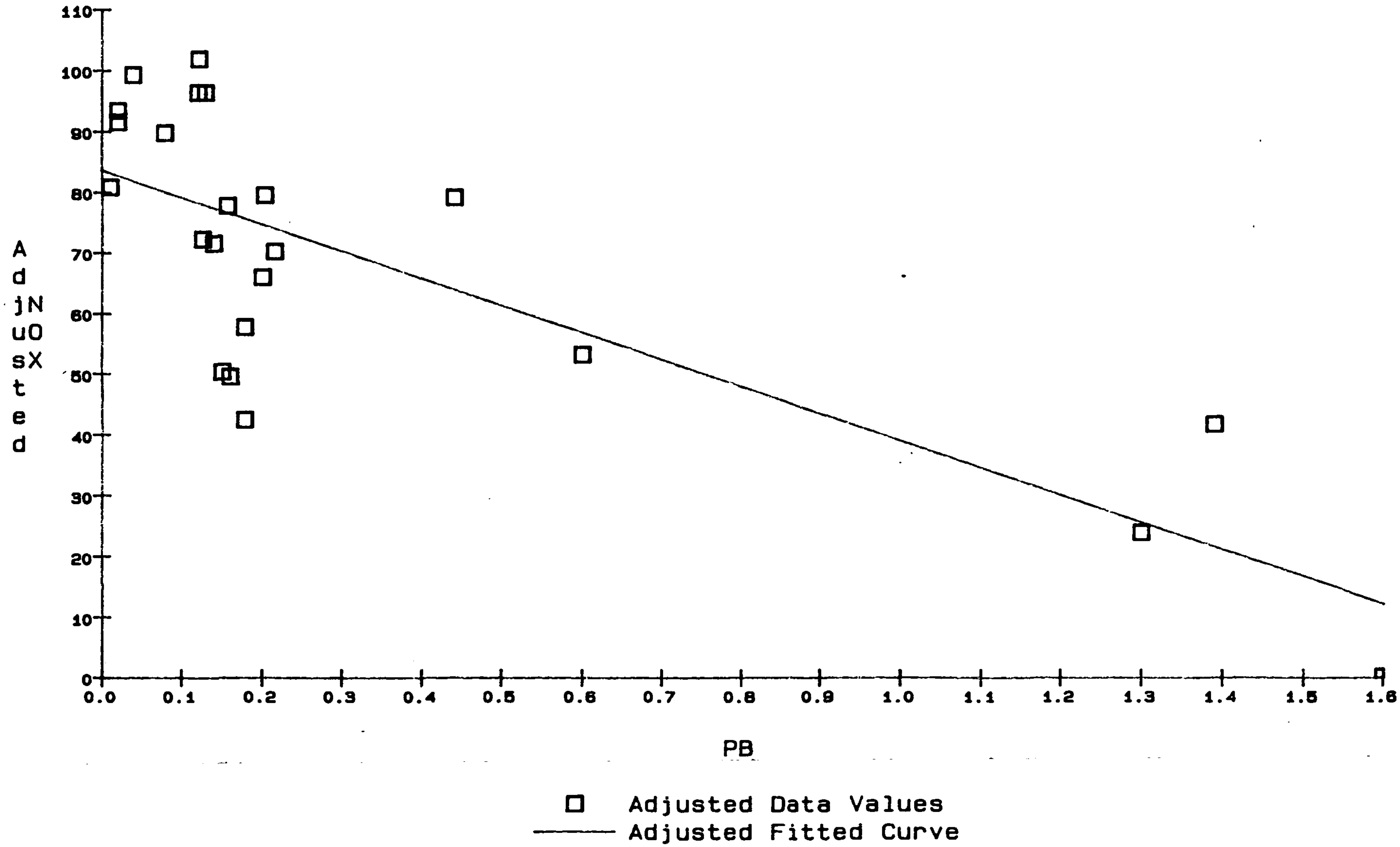


FIGURE 17

Graph: 49307

08-AUG-90 13:27 Page 1

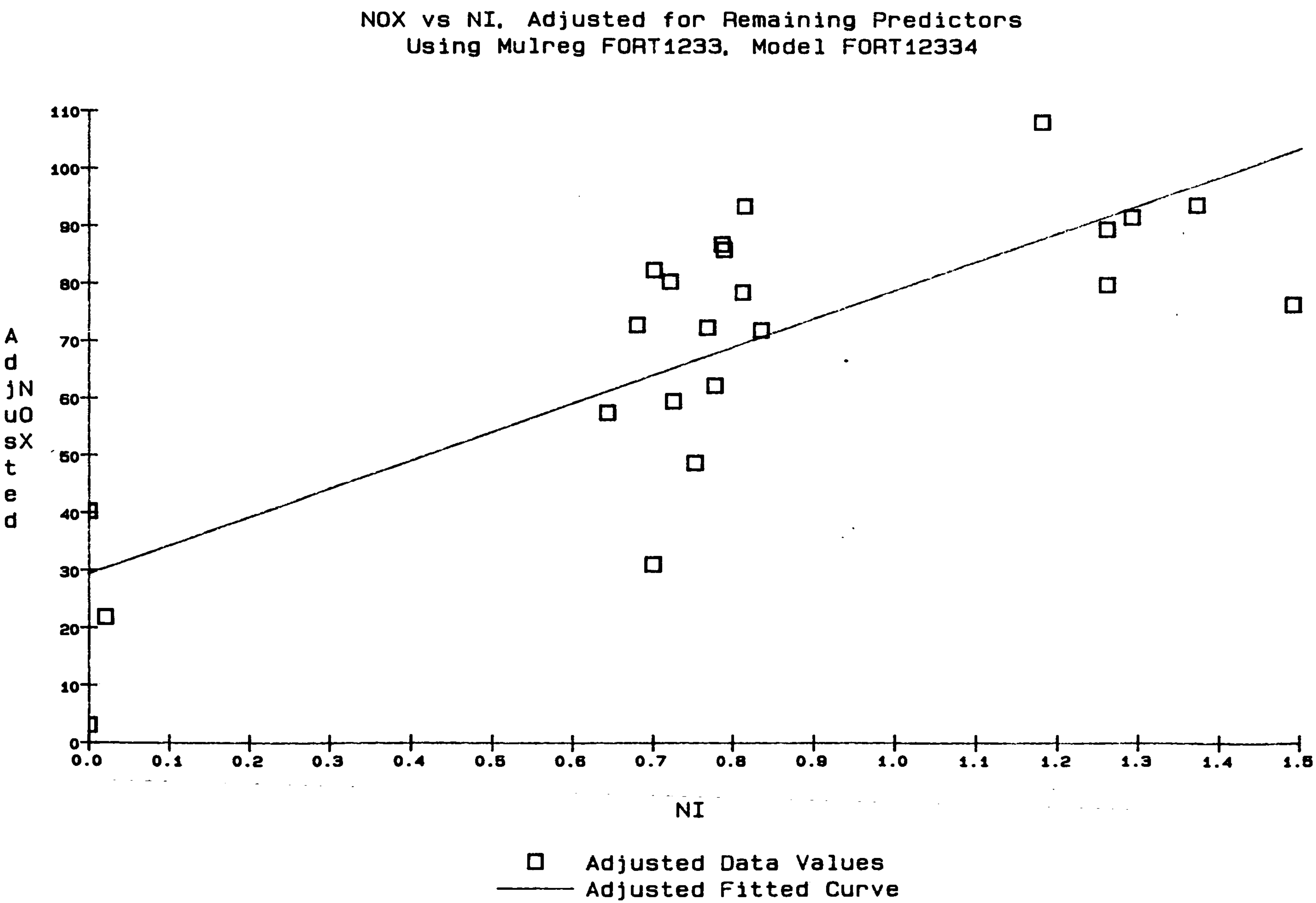


FIGURE 18

Graph: 49298 08-AUG-90 13:27 Page 1

NOX vs M2_G, Adjusted for Remaining Predictors
Using Mulreg FORT1233, Model FORT12334

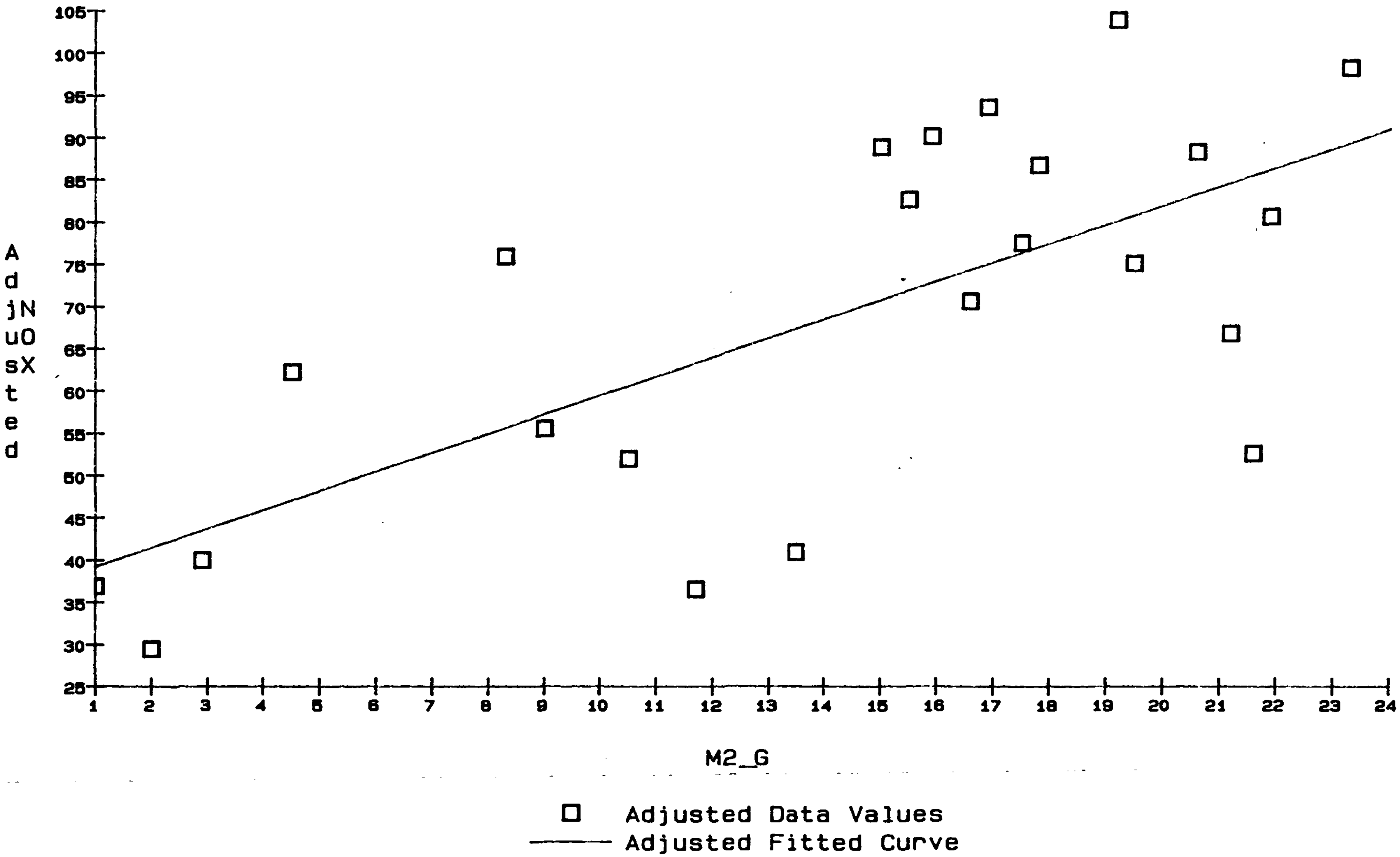


FIGURE 19

Graph: 49316

08-AUG-90 13:29 Page 1

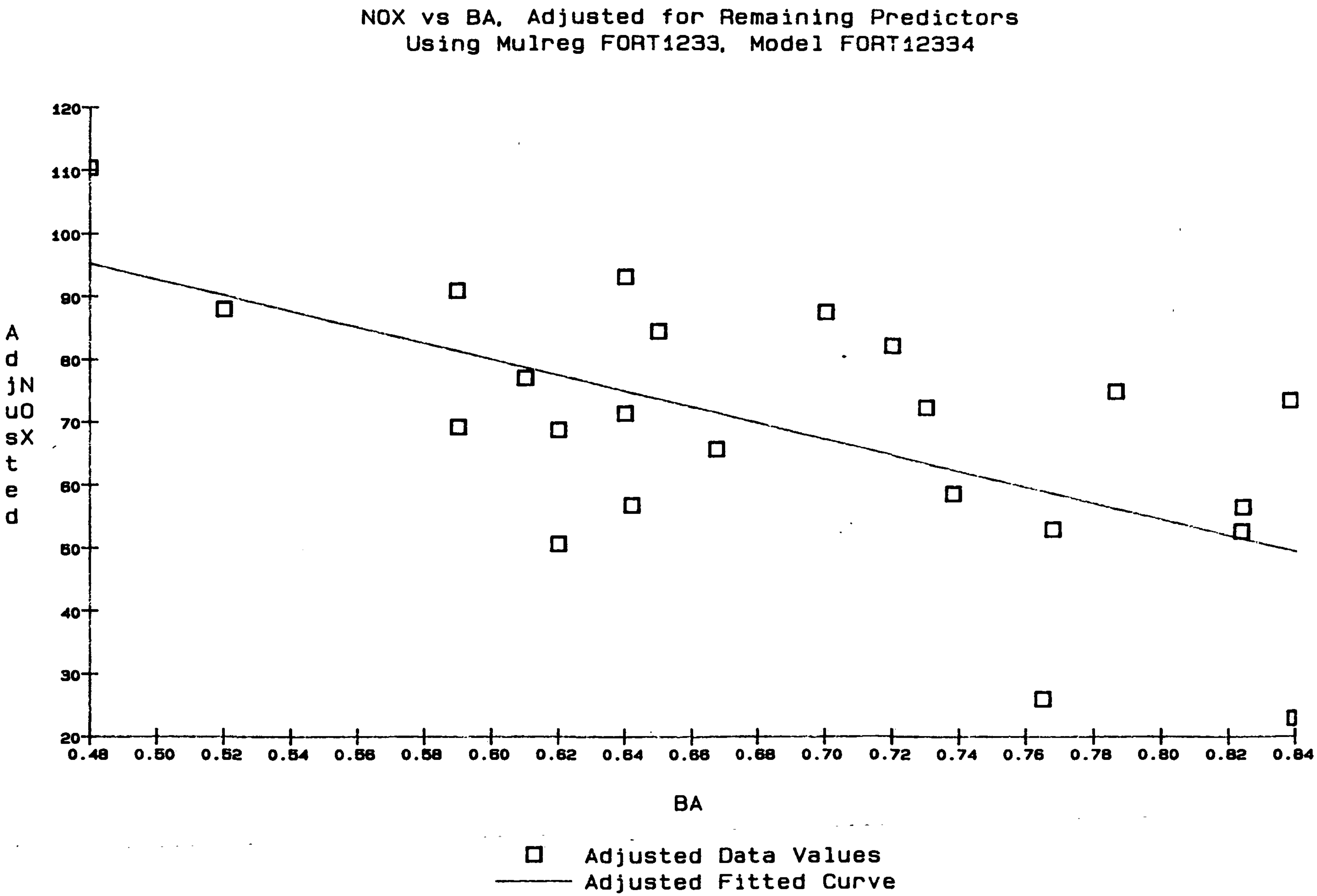
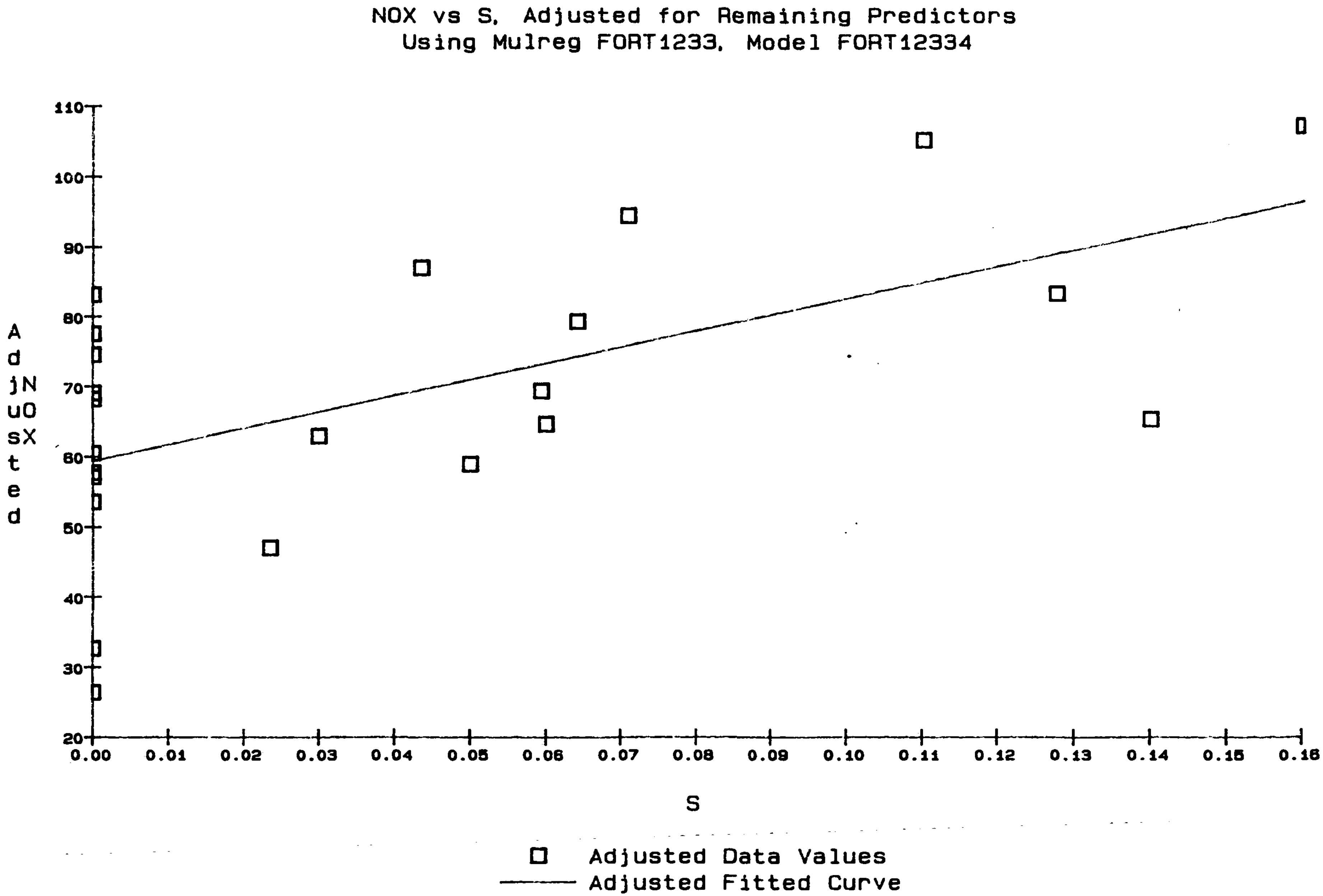


FIGURE 20

Graph: 49334 08-AUG-90 13:31 Page 1



5

Response to MECA Comments on Ethyl's Waiver Request for HiTec 3000

Prepared by Charles M. Heinen, Consultant

Comments were submitted by MECA on July 19,1990 to the honorable William Reilly EPA Administrator on the subject of a fuel additive containing methylcyclopentadienyl manganese tricarbonyl (MMT) at the manganese level of 1/32 gram/gallon of unleaded gasoline. Ethyl Corp. has requested a waiver to market this fuel additive for unleaded gasoline under the trade name of HiTec 3000.

MECA indicated that there are five adverse effects from the combustion products of manganese which apparently worry their "catalyst experts".

1. Coating of active catalyst sites
2. Plugging or clogging of the small flow channels of a monolith catalyst.
3. Chemical reactions which reduce the catalyst surface area.
4. Deterioration and reduced thermal durability of ceramic substrates
5. Interference with improvements in precious metal/support interactions.

These fears include those expressed by other submittors in writing, and this response will include portions of their documents where appropriate.

Subjects 1 and 2 will be combined under the title of "Plugging of Active Catalyst Cites". Subjects 3 and 4 also will be combined under "Chemical Reactions, including those of Mn, which could affect catalysts".

Subject 5 is difficult for me since I am not gifted at clairvoyance or necromancy, but perhaps my views of "The future" will interest MECA and EPA.

Plugging of Active Catalyst Cites

The MECA comments on this subject are general and vague. For technical back-up they submitted a recent paper by Hurley et.al[1]

Response to MECA Comments on Ethyl's Waiver Request for HiTec 3000

Prepared by Charles M. Heinen, Consultant

Abstract

A response to the MECA comment was prepared using industry data submitted to E.P.A. on the subject of HiTec 3000 and additional published information from the technical literature.

The analysis reported herein shows that at the exhaust temperatures of operation of the vehicles which were analyzed, the Mn exhausted from HiTec 3000 is in the form of Mn_3O_4. In this form it does not enter into chemical reactions with catalyst components. It forms a randomly distributed coating which becomes modestly thicker linearly with mileage. The deposit is porous and does not affect exhaust reactions. The vehicles used for calculations were all Canadian, and all contained manganese, therefore, it was assumed that the level used for fueling was 1/16 gram per gallon or twice the level proposed in the HiTec 3000 waiver request.

Several reactions of Mn_3O_4 with catalyst components were postulated by MECA. All occurred at temperatures above which the catalysts suffer drastic decreases in surface area and catalyst activity so these reactions were not explained.

Several catalyst showed drastic losses in surface area and reactivity. The general subject of thermal reactions and their causes that might have resulted in the failures is discussed.

Some speculation on the future using appropriate obfuscation is included.

from the Ford Motor Co. Their paper contains much of the type of technical information required to assess the role of the MMT additive in actual field operation. With the exception of the voluminous work by Ford reported in their submission of July 23, 1990 to docket no. A-90-16, there is little in the literature that permits analysis of the role, if any, of MMT in catalyst failures. These papers are a treasure trove for anyone interested in the subject.

Attachment 1 of the Ford submission details the test performed on 11 catalysts from ten vehicles driven normally by Ford of Canada employees. None had reported operational or mechanical problems. The vehicles were fueled with commercially available Canadian fuel presumably containing about 1/16 g Mn/Gal. In accordance with levels allowed by Canadian law (the Ethyl waiver request is for 1/32g Mn/Gal.) Ford states, and we agree that the contaminants in deposits on the catalysts, such as Pb, S, P, and Zn are within normal ranges. None of the catalyst showed any sign of thermal distress, in short this should be a normal customer fleet. It will be referred to as "11 Catalyst Fleet".

The second fleet contained 9 vehicles, some with single and others with double brick configurations. As a result it yielded 15 catalysts. Nevertheless, it is referred to as the "9-Catalysts Fleet" in this document. The catalysts in this fleet were removed because of suspected catalyst defects. No information was submitted on the fueling characteristics of the fleet. Therefore, it was concluded by the authors, and necessarily by me that normal Canadian fuel containing 1/16 gMn/gal as MMT was used. The fleet was the subject of the paper by Hurley et.al. referred to above. One apparent over temperature condition was observed in one catalyst, but no other signs of catalyst damage were observed. Compared to Fleet Eleven, the catalysts appear to have suffered moderately severe treatment.

The third fleet contained 26 catalysts from 13 vehicles. All were of the two brick configuration. (Each brick is treated separately.) It is referred to in this document as the "26 Catalyst Fleet".

The converters in this fleet were sent in because of "poor performance" and/or driveability problems. As in the previous vehicle set, <u>no information</u> on fuels used was available so 1/16 g Mn was assumed. In one catalyst (#100) there were indications of severe over-temperature conditions. The rear portions of bricks 1 and 2 were broken and melted according to the Ford report. In another, there was only one brick and it had been reduced to baseball size, presumably as the result of abrasion. A third (#103) had an incomplete data set. A fourth catalyst (#106) had all the indications of a nearly new catalyst even though the vehicle had 33,000 mile. Consequently, the data from 102,103 and 106 were not used in our data analysis. The conditions in this fleet appear to have been severe.

All reports from the auto companies and others agree that the catalysts are covered with a reddish coating of varying thickness which sometiumes leads to erroneous first impressions. The Hurley et.al report on page 5 is more detailed, specifically they state:

> These results confirm earlier experimental results (3,5) in that the Mn derived from MMT is converted in the combustion process exclusively to Mn_3O_4
>
> Optical micrographs (figures 3 and 4) of catalysts, 301G and 301I, show a heavy residual layer covering the washcoat. X-Ray fluorescence results indicate that these two samples, contain approximately 4 and 6 wt% of Mn, respectively and are from vehicles with 22,000 and 33,000 accumulated in-use miles. As is evident in both of the high magnification micrographs, from 301G and 301I, the Mn_3O_4 is on layered on the surface of the washcoat. It does not appear to penetrate or have reacted with the washcoat but simply adheres to the surface. This deposit of Mn_3O_4 on the washcoat may cause physical pore plugging and thus result in mass-transfer problems.
>
> Scanning Electron Microscopic and Electron Probe analysis show the thickness of the Mn_3O_4 residual layer to range from approximately 5 microns to a maximum of approximately 20 microns. The thickest layer is observed on catalyst 301I which had 33,000 accumulated

> miles. SEM micrographs (figure 5) of cross-sections of 301G and 301I show this layer quite distinctly. Also shown in this figure is a Mn x-ray elemental map pattern to confirm that the layer is indeed rich in Mn. This elemental map is used to determine the actual thickness of the Mn rich region on the washcoat. This micrographs also indicate little if any penetration into the washcoat by the Mn rich layer. Indications from the surface morphology study is that the Mn rich layer does simply adhere to the surface of the washcoat. An example of the surface morphology of the Mn rich layer is shown in figure 6. As is shown in the micrograph the surface is covered with a layer of fluffy, porous material. This material was confirmed by XRD to consist exclusively of Mn_3O_4.

The underlining is not in the original text. These comments were valuable for evaluating the qualitative information supplied by Ford and others. The comments and quantitative data supplied by Ford were used extensively in order to answer the following questions:

A. Do the Mn_3O_4 deposits continue to grow with exhaust flow or do they reach an equilibrium level?
B. Are the deposits stable (on the surface) or do they react?
C. Are the deposits truly porous or do they restrict the the catalyst effectiveness?

Question A

Ford did extensive X-ray fluorescence analyses of the components and the contaminants. They sectioned the various bricks and obtained the composition of each, so that 3 analyses are available for each brick of the 9-catalyst fleet and the 26 catalyst fleet. The data were analyzed to determine whether averaging the three sections yielded substantially different results than the averages when compared with other variables. They did not. Apparently, Ford reached the same conclusion because the 11 Catalyst Fleet paper reported only single numbers for consistency and simplicity. All graphs in this presentation use only averages where more that one number is available for a single brick.